Preparation of Copolymeric Gels Composed of Polydimethylsiloxane and Polyethylene Oxide Network Chains and Their Specific Characteristics

Shinzo Kohjiya,* Hideki Tsubata, and Kenji Urayama

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

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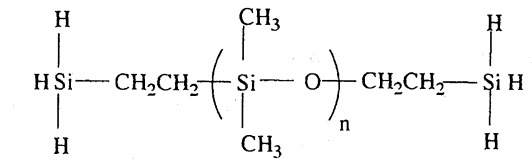
Copolymeric networks composed of two chemically different network chains, polydimethylsiloxane (PDMS) and polyethylene oxide (PEO), are prepared by the two synthetic methods: (1) Vinyl-terminated PDMS and PEO are end-linked with the multi-functional silane compounds; (2) Vinyl-terminated PEO and silyl-terminated PDMS are end-linked with each other. The compositions in the resulting two-component networks are determined by two independent methods: ^{1}H NMR analysis of the extracted unreacted materials and thermogravimetric analysis of the network samples. The appearances of the copolymeric networks are transparent. The differential scanning calorimetry and dynamic mechanical analysis show that the copolymeric networks have the microphase separated structures composed of PDMS and PEO phases. Swelling experiments in various solvents clearly indicates the amphiphilic character of the copolymeric networks. The Li-doped copolymeric networks, which are obtained by immersing the gels in $LiClO_4$, exhibit conductivity of the order of 10^{-6} S cm^{-1} at room temperature. The temperature dependence of the conductivity obeys the William–Ferry–Landel equation based on the free volume theory.

The polymer network systems composed of (more than) two kinds of components different in physicochemical properties have been expected to be promising functional polymeric materials.[1—3] The attempts to connect some different chemical components by chemical bonds were first made for the copolymers made of multi-components with block- or random sequences.[4,5] The introduction of crosslinkage gives the systems rubber elasticity and swelling ability which can not be seen in the uncrosslinked systems. The polymer network systems composed of two kinds of polymeric components can be divided into the following three groups on the basis of network topology: interpenetrating networks (IPNs) in which the two independent networks composed of each component are topologically interpenetrated with each other; semi IPNs in which one component is the crosslinked network, and the other is the uncrosslinked polymer; copolymeric networks in which the network chains consist of two kinds of components. This study is concerned with the third type, especially the copolymeric networks in which *one polymeric component corresponds to the constituent between the adjacent crosslinks (i.e. a network chain itself)*.

In this study, polydimethylsiloxane (PDMS) and polyethylene oxide (PEO) have been employed as the components of the copolymeric networks. PDMS is a hydrophobic polymer which possesses both inorganic and organic characters, and shows good performance in heat-resistance, oxygen-permeability, lubricity, and electro-insulation.[6] Due to such good performances, PDMS has often been used as a component in polymer alloys and blends aiming at functional polymeric materials.[4,5] PEO is a hydrophilic polymer which has good biocompatibility and ionic conductivity. Especially, compounds of PEO and alkaline metal salt have been widely investigated as a promising polymeric solid ion conductor.[7—12] The copolymeric networks composed of PDMS and PEO components which show some good performances solely are expected to have the wide applicability to industrial uses as a multi-functional polymeric material. In this study, the amphiphilic and ion-conductive characters of the PDMS–PEO copolymeric networks have been demonstrated. The amphiphilic properties of the copolymeric networks have been examined by the swelling experiments in the solvents with a series of solubility parameters. The conductivity of the Li-doped copolymeric networks has been investigated as a function of temperature.

It it well known that physicochemical properties of multicomponent polymeric systems strongly depend on the morphology and structures. In the case of copolymeric networks, since the preparation schemes involve the reaction between two chemically different polymers, the preparation methods may influence the details of the structure of the resulting networks such as the compositions and sequences of the components. The preparation schemes for copolymeric networks which have been reported so far can be roughly classified into the following two groups: (A) Reaction between bifunctional telechelic polymers, and the polymers having multifunctional sites at the side chains;[13—16] (B) Reaction between bifunctional and multifunctional telechelic polymers.[17] The networks prepared by scheme (B) have more definite structures relative to those by scheme (A), since the crosslinking in scheme (B) is made by so-called end-linking reaction, by which a network chain between the adjacent crosslinks is equivalent to a precursor telechelic polymer. Accordingly, the scheme (B) is more suitable for the purpose of the clarification of the correlations be-



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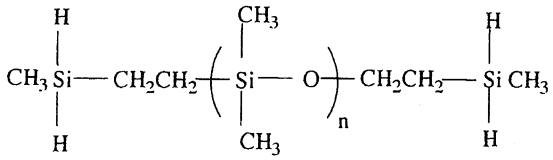
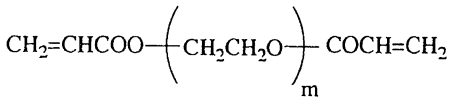


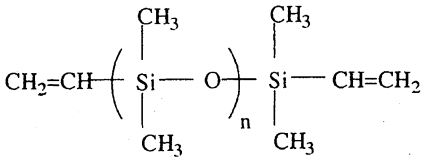
HST-PDMS

+



AT-PEO

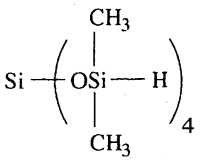
Scheme 1.



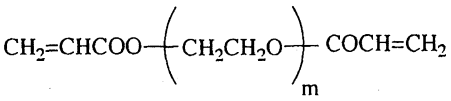
VT-PDMS

AND

+



TDMS



AT-PEO

Scheme 2.

tween the physical properties and the network structures. However, there is only one study[17] in which scheme (B) is employed. In this study, we have prepared the copolymeric networks on the basis of scheme (B) by means of the

following two types of hydrosilylation: (I) the end-linking reaction between silyl-terminated PDMS and acrylate-terminated PEO (Scheme 1); (II) the end-linking reaction between vinyl-terminated PDMS and acrylate-terminated PEO with multi-functional silane compound (Scheme 2). The compositions and physicochemical properties for the copolymeric networks prepared by Schemes 1 and 2 have been investigated, and the effects of both the schemes on those properties have been discussed. The morphology and structures of the copolymeric networks have been estimated on the basis of the experimental results of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

Experimental

Materials. Vinyl-terminated PDMS (VT-PDMS) (Nihon Unikar Co.) and acrylate-terminated PEO (AT-PEO) (Shin-Nakamura Kagaku Co.) were employed as precursor polymeric chains. Three kinds of VT-PDMS (VS1, VS2, and VS6) and AT-PEO (E3, E5, and E7) different in molecular mass were used. The number- and weight-average molecular weights of each precursor chain, which were determined by gel permeation chromatography (GPC), are listed in Table 1.

Tris(dimethylsiloxy)phenylsilane (PhTDMS) (Chisso Co.) and tetrakis(dimethylsiloxy)silane (TDMS) (Chisso Co.) were used as crosslinkers for end-linking VT-PDMS and AT-PEO by Scheme 2. Diethoxymethylsilane (DEMS) (Shinetsu Chemical Co.) and triethoxysilane (TEOS) (Tokyo Kasei Co.) were employed in the reactions for converting the vinyl groups in VT-PDMS into silyl and monosubstituted silyl terminated ones for Scheme 1, respectively.

Chloroform, tetrahydrofuran (THF), toluene, 1,4-dioxane, and diethyl ether were used as solvent after distillation.

Spier's catalyst ($H_2PtCl_6 \cdot 6H_2O$) diluted by THF was employed as catalyst for hydrosilylation reaction.

Analysis of Hydrosilylation of a Mixture of VT-PDMS and AT-PEO. The hydrosilylation of a mixture of VT-PDMS (VS1) and AT-PEO (E7) with PhTDMS was performed in protonated chloroform at 60 °C using Spier's catalyst. The catalyst concentration was 5.58×10^{-4} mol dm^{-3}. ^{1}H NMR and GPC analysis were done for the solutions extracted from the reaction bath before reaction ($t = 0$) and at $t = 120$ min. The reaction conditions for each sample are shown in Table 2.

Table 1. Number- and Weight-Average Molecular Weights (M_n and M_w, Respectively) for VT-PDMS and AT-PEO

Sample	M_n (g mol^{-1})	M_w (g mol^{-1})
VS1	870	1300
VS2	2800	4600
VS6	6000	9600
E3	380	460
E5	550	630
E7	620	680

Synthesis of Silyl-terminated PDMS. Silyl-terminated PDMS (HST-PDMS) for Scheme 1 was synthesized by Scheme 3. The synthesis for hexa-functional HST-PDMS was done as follows. The mixture of VT-PDMS and TEOS with the molar ratio 0.46/1 was dissolved in toluene, and Spier's catalyst was added to the solution. Hydrosilylation was carried out at 80 °C for 48 h, and thereafter unreacted TEOS was removed by evaporation. The remains were dissolved in diethyl ether with $LiAlH_4$, and the solution was stirred for 7 h. HST-PDMS was obtained by evaporating the solvent from the solution after filtration. Tetrafunctional HST-PDMS was acquired in a similar way, using DEMS instead of TEOS. The quantitative conversion of vinyl groups into silyl ones were confirmed by ^{1}H NMR and IR analysis. The GPC of VT-PDMS and the resulting HST-PDMS coincided, indicating that the breaking of the backbone (–Si–O–) did not occur through the reactions. We designated the *f*-functional HST-PDMS prepared from VS*x* as HS*x*–*f*.

Preparation of Copolymeric Networks. Copolymeric networks were prepared by the two methods, i.e., Schemes 1 and 2. In both Schemes 1 and 2, the materials were dissolved in dioxane with Spier's catalyst. The solution was transferred to Teflon® mold ($25 \times 40 \times 10$ mm). The hydrosilylation was performed by keeping the mold at 80 °C while evaporating the solvent. PDMS networks were made by hydrosilylation between hexafunctional HST-PDMS and VT-PDMS, and PEO networks were prepared by the reaction between E7 and TDMS. The preparation conditions of each sample are shown in Table 3. The sample code HS1-4-E3 means the copolymeric network which was made from HS1-4 and E3 through Scheme 1. The sample code VS1-E3 shows the copolymeric network which was prepared from VS1 and E3 with TDMS through Scheme 2. HS1-VS1 and GE7 represent the PDMS network made using HS1-6 and VS1, and the PEO network prepared from E7, respectively.

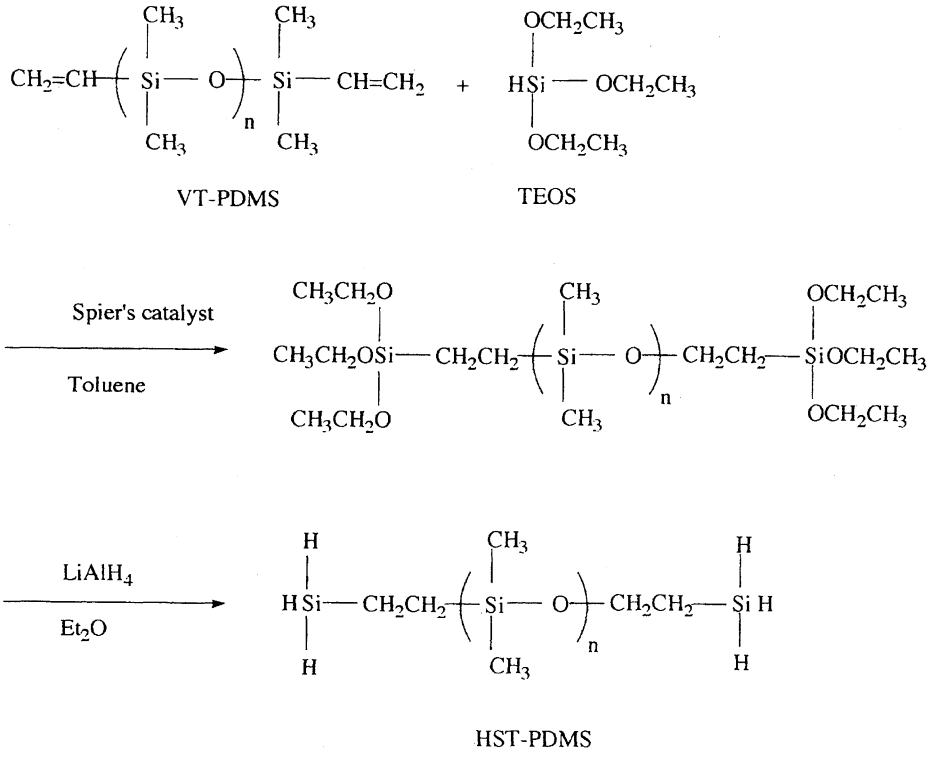
The resulting network samples were immersed in THF, which is a good solvent for PDMS and PEO, for two days in order to extract unreacted materials. The solutions containing the unreacted materials were analyzed by ^{1}H NMR in order to determine the contents of PDMS and PEO incorporated into the networks.

The ion-conductive gels were prepared as follows. After the extraction procedure, the swollen samples were completely dried, and the weights of the dry samples were measured. The dry samples were immersed in THF containing a certain amount of $LiClO_4$ for two days. Subsequently, the swollen samples were fully dried under reduced pressure, and the dried samples were weighed. The amount

Table 2. Reaction Conditions and Degrees of β-Addition and Hydrogenation in Hydrosilylation of Mixtures of VT-PDMS and AT-PEO with PhTDMS

Sample	[VT-PDMS]	[AT-PEO]	r[a)]	VT-PDMS		AT-PEO	
				β-Addition	Hydrogenation	β-Addition	Hydrogenation
	(mol dm^{-3})	(mol dm^{-3})		%	%	%	%
E0-07	0.050		0.74	60.5	1.5		
E33-05	0.033	0.015	0.53	53.2	0	23.5	10.1
E50-05	0.024	0.023	0.54	50.9	0	9.3	47.7
E100-07		0.048	0.72			1.2	30.6

a) r = [Si–H]/[C=C].



Scheme 3.

Table 3. Preparation Condition of Copolymeric Gels

Sample	HST-PDMS	VT-PDMS	AT-PEO	TDMS	r[a)]	Catalyst
	mmol	mmol	mmol	mmol		10^4 mmol
HS1-4-E3	0.460		0.920		1.0	6.78
HS1-4-E5	0.258		0.518		1.0	6.78
HS1-4-E7	0.267		0.532		1.0	6.78
HS1-6-E3	0.309		0.917		1.0	6.78
HS1-6-E5	0.231		0.700		1.0	6.78
HS1-6-E7	0.186		0.532		1.1	6.78
HS2-6-E5	0.203		0.600		1.0	4.52
HS2-6-E7	0.193		0.565		1.0	3.39
HS6-6-E5	0.072		0.219		1.0	6.78
VS1-6-E3		0.325	1.29	0.814	1.0	6.67
VS1-6-E5		0.272	0.800	0.533	1.0	6.67
VS1-6-E7		0.206	0.608	0.413	1.0	6.67
VS2-6-E5		0.234	0.700	0.567	1.2	10.0
VS2-6-E7		0.192	0.563	0.385	0.99	15.0
HS1-4-S1	0.223	0.488			0.91	6.78
HS1-6-S1	0.225	0.506			1.3	6.78
HS2-6-S2	0.087	0.267			0.98	6.78
GE7			1.01	0.501	1.0	2.23

a) r = [Si–H]/[C=C].

of $LiClO_4$ incorporated into the samples were determined from the increase in the dry weight.

Apparatus. ^{1}H NMR analysis was done at room temperature by Hitachi R-1100 and Varian XL-200.

GPC measurements were performed by Shimadzu LC-6A equipped with a UV detector. The column temperature was 40 °C, and the flow rate was 1 ml/min. Chloroform was used as carrier solvent.

The thermogravimetric analysis (TGA) of copolymeric networks was made by means of Thermoflex TG-8100 (Rigaku Denki Co.). The differential scanning calorimetry (DSC) of the samples was carried out by using Thermoflex DSC-8230 (Rigaku Denki Co.). The TGA and DSC measurements were done under N_2 atmosphere at the heating rate of 10 °C min^{-1}.

The dynamic mechanical analysis (DMA) of the samples were conducted by means of DVE-V4 (Reoroji Co.). The measurements were made under shear oscillation at the frequency of 10 Hz and at the heating rate of 2 °C min^{-1}.

The ionic conductivity of the samples was measured in a glass vessel equipped with a temperature controllable heater under N_2 atmosphere by means of LF impedance analyzer 4192A (Yokokawa Hewlett Packard Co.). Platinum electrodes were used. The measurements were done at the frequencies ranging from 5 Hz to 1 MHz. The details of the measurements for ionic conductivity are provided elsewhere.[12]

Results and Discussion

Characterization of Hydrosilylation for Mixtures of VT-PDMS and AT-PEO. The hydrosilylation processes of the mixtures of VT-PDMS and AT-PEO with a series of mixing ratios were characterized by ^{1}H NMR.[19] Figure 1 shows the ^{1}H NMR spectra of the mixture E33-05 before reaction (Fig. 1(a)) and at $t = 120$ min (Fig. 1(b)). The assignments of each peak are also indicated in the figure. The degrees of conversion for vinyl groups in VT-PDMS and AT-PEO (p_{vt} and p_{at}, respectively) were evaluated as follows. p_{at} was obtained from the decrease in the area of the peaks (e) assigned to the protons in vinyl groups in AT-PEO. The peak area for the protons in vinyl groups for unreacted VT-PDMS was obtained by subtracting the area of peak (d) from the areas of the peaks overlapped by (a), (b), and (d). The area of peak (d) was evaluated to be twice as large as the one of peak (e) on the basis of the ^{1}H NMR spectrum of unreacted AT-PEO alone. The area of peak (f) was used as the standard for the calculations for p_{vt} and p_{at}. The occurrence of the hydrogenation as a side reaction was observed by the emergence of peak (*m*), in addition to the normal β-addition reaction (i.e., hydrosilylation). The degrees of β-addition and hydrogenation for each sample are listed in Table 2. It is found that the β-addition proceeds quantitatively in VT-PDMS, while the hydrogenation occurs prior to the β-addition in AT-PEO. The hydrogenation results from the reaction between an intermediate product in hydrosilylation and a nucleophilic substance such as water and alcohol. The hydrogenation in this study should be caused by water which could not be removed in pre-drying AT-PEO. It is in general difficult to remove water completely from hydrophilic polymers. The effects of substituents on the reactivity of vinyl groups in hydrosilylation were investigated for low molecular mass substances by Lewis.[20] He reported that the rate of reaction for the electron-releasing substituents is larger than that for the electron-withdrawing ones. On the basis of his results, the lower reactivity of AT-PEO should be mainly attributed to the electron-withdrawing character of carbonyl groups adjacent to vinyl groups. The reactivity of vinyl groups in AT-PEO is considerably depressed due to the electron-withdrawing character of carbonyl groups; thereby, AT-

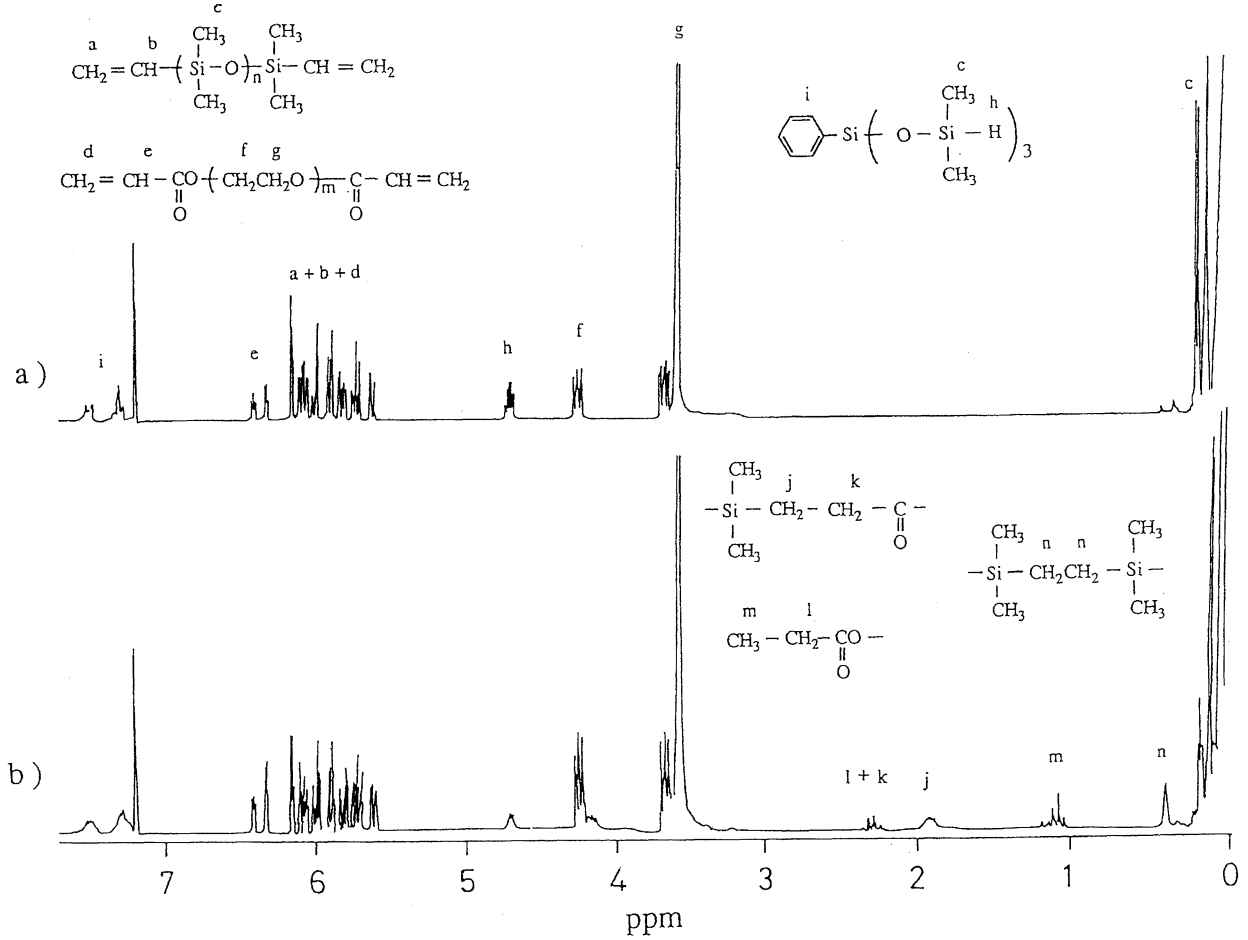


Fig. 1. ^{1}H NMR spectra of the mixture E33-05 before reaction (a) and at $t = 120$ min (b).

PEO should become susceptible to hydrogenation as a side reaction.

Composition of Copolymeric Networks. Table 4 shows the amounts of unreacted materials and the compositions of copolymeric network samples which were determined by the ^{1}H NMR analysis of the solutions containing the extracted (unreacted) materials. The weight fractions of PEO determined by TGA analysis for the copolymeric networks are also indicated. TGA measurements showed that the starting temperatures for the decomposition of copolymeric networks were ca. 50—80 °C lower than the one for the PDMS networks. The decrease in weight within the temperature range between the starting temperatures for the decomposition of the PDMS networks and the copolymeric networks was considered to be equivalent to the weight of PEO in the copolymeric networks. The excellent agreement in the weight fractions of incorporated PEO determined by ^{1}H NMR and TGA can be seen in Table 4. This result indicates the high reliability for the compositions obtained by these measurements. It is in general difficult to determine the composition of gels by direct measurements such as ^{1}H NMR due to their insolubility against solvents, apart from the gels to which FT-IR analysis is applicable.[15] The two methods shown here can be reliable measurements for the compositions of multicomponent networks.

The weight fractions of unreacted materials for all the samples were not so small (larger than 10 wt%), indicating that the hydrosilylation did not proceed quantitatively. The following two factors are considered as the obstacles for the quantitative hydrosilylation: A finite degree of hydrogenation as a side reaction caused by water which was not removed in pre-drying, which was demonstrated in the previous section; The reaction system is the one between the hydrophilic and hydrophobic polymers much different in polarity, resulting in a low miscibility. It is also found in Table 4 that the amount of not-incorporated AT-PEO is larger than the amount of not-incorporated VT-PDMS for all the samples. This result is explained by the foregoing result for the characterization of hydrosilylation for the mixture of AT-PEO and VT-PDMS: The hydrogenation occurs prior to hydrosilylation in AT-PEO, and the resultant hydrogenated AT-PEO can not be incorporated into the networks.

It should be noted that the amounts of unreacted materials for the samples by Scheme 1 are smaller than those by Scheme 2, when the comparisons are made for the networks in which the components have the identical molecular masses. A significant difference in Schemes 1 and 2 is that in Scheme 2 the networks can be formed by crosslinking VT-PDMS alone without AT-PEO. Due to this difference, in addition to the above-mentioned lower reactivity of AT-PEO for hydrosilylation, the chance for the hydrosilylation of AT-PEO would be more reduced in Scheme 2.

DSC and DMA Analysis. The appearances of all the copolymeric network samples except HS1-4-E7 are transparent, meaning that PDMS and PEO components in these samples are miscible at least in the spatial order more than a few thousand Å corresponding to the wavelength of visible rays. The appearance of HS1-4-E7 is cloudy (not entirely opaque), showing that a finite size of microphase separated structure is formed. In order to investigate the phase structure of the copolymeric networks in more detail, we have performed the DSC and DMA analyses.

Figures 2 and 3 show the DSC thermograms for HS1-4 and VS1-6 series samples, respectively. Figures 4 and 5 indicate the temperature dependence of storage shear modulus (G') and loss tangent (tan δ) for HS1-4 and VS1-6 series samples, respectively. Table 5 indicates the glass transition temperatures (T_g) assigned to PDMS and PEO for each sample obtained by DSC and DMA. The two independent glass transitions corresponding to the PDMS and PEO phases were observed in the DSC curves and the temperature dependence of tan δ for all the copolymeric networks, which suggests that the copolymeric networks in this study have the microphase-separated structure composed of the PDMS and PEO phases.

Table 4. Weight fraction of Total Extracted Materials (w_{sol}), Weight Fractions of Extracted PDMS, PEO, and the PEO Content in Copolymeric Networks

Sample	w_{sol}	Extracted PDMS	Extracted PEO	PEO content in copolymeric gel	
	wt%	wt%[a)]	wt%[a)]	wt%[b)]	wt%[c)]
HS1-4-E3	16.6	2.6	39.2	27.8	28
HS1-4-E5	35.3	9.6	46.7	38.1	38
HS1-4-E7	39.8	4.7	57.6	41.0	41
HS1-6-E3	21.9	0	44.7	34.7	35
HS1-6-E5	35.5	0	42.5	48.5	48
HS1-6-E7	36.8	11.4	48.3	55.3	55
VS1-6-E3	28.6	18.3	42.5	33.0	33
VS1-6-E5	46.3	33.8	60.5	35.6	36
VS1-6-E7	53.7	43.3	54.3	56.9	57
HS2-6-E5	15.6	5.1	29.1	35.7	35
HS2-6-E7	12.1	3.5	19.4	46.1	46
VS2-6-E5	47.8	29.6	56.9	28.9	29
VS2-6-E7	43.5	30.0	39.2	47.0	47

a) [Extracted]/[Feed]. b) Determined by GPC analysis of solutions containing extracted materials. c) Determined by TGA of copolymeric gel.

Table 5. Glass Transition Temperature (T_g) of PDMS and PEO Phases in Copolymeric Gels

Sample	PEO content	T_g of PDMS phase (°C)		T_g of PEO phase (°C)	
	wt%	(DSC)[a]	(DMA)[b]	(DSC)[a]	(DMA)[b]
HS1-4-S1	0	−114			
HS1-4-E3	28	−100	−82	—[c]	42
HS1-4-E5	38	−105	−86	−37	−16
HS1-4-E7	41	−105	−84	−41	−14
HS1-6-S1	0	−112	−96		
HS1-6-E5	48	—[c]	—[c]	−37	−18
HS1-6-E7	55	—[c]	—[c]	−43	−10
VS1-6-E3	33	−99	−86	2	20
VS1-6-E5	36	—[c]	−71	—[c]	−10
VS1-6-E7	57	−108	−92	−45	−12
HS2-6-S2	0	−120	−110		
HS2-6-E5	36	−115	−100	−36	−18
HS2-6-E7	46	−119	−116	−41	−26
VS2-6-E5	29	−117	−98	—[c]	−32
VS2-6-E7	47	−118	−112	−46	−32

a) The temperature at the midpoint in abrupt change in DSC thermogram. b) The temperature at the peak of tan δ.
c) Unable to determine due to a broad transition.

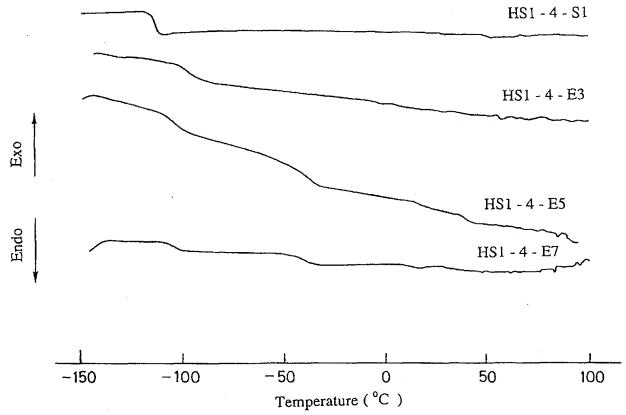


Fig. 2. DSC thermograms of HS1-4 series.

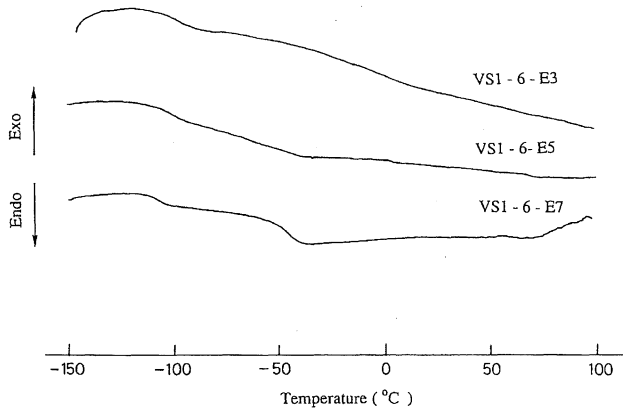


Fig. 3. DSC thermograms of VS1-6 series.

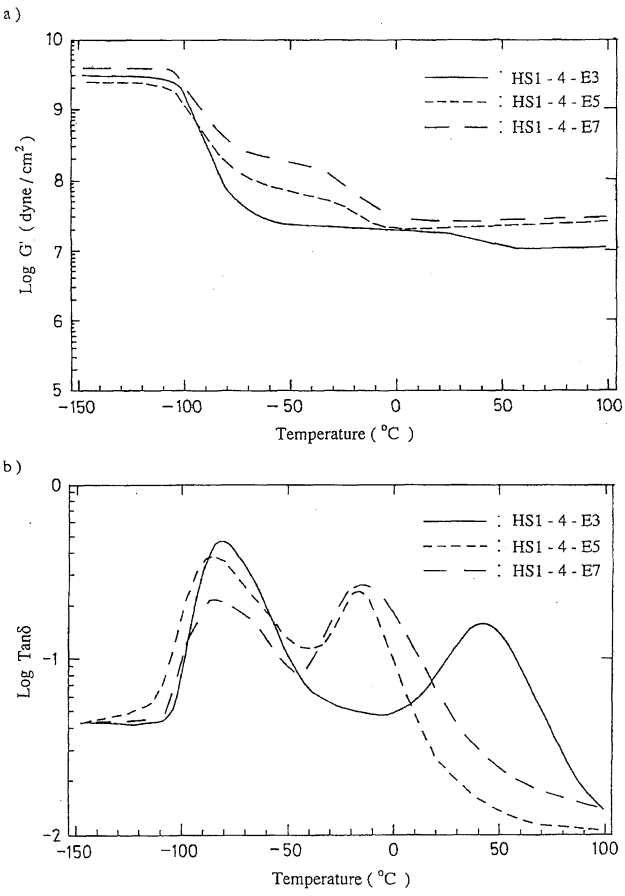


Fig. 4. Temperature dependence of G' (a) and tan δ (b) for HS1-4 series.

It is found that T_g's for the PDMS component with M_n=870 in the copolymeric networks are ca. 10—15 °C higher than T_g for the corresponding PDMS network, regardless of preparation method for copolymeric networks. On the other hand, T_g's for the PDMS component with M_n = 2800 in the copolymeric networks are almost the same as T_g values for the corresponding PDMS networks. Furthermore, the peak for the glass transition for PDMS component with M_n = 870 is broader than the one for PDMS component with M_n=2800. These results suggest that the PDMS components with M_n = 870 are partially miscible with the PEO compo-

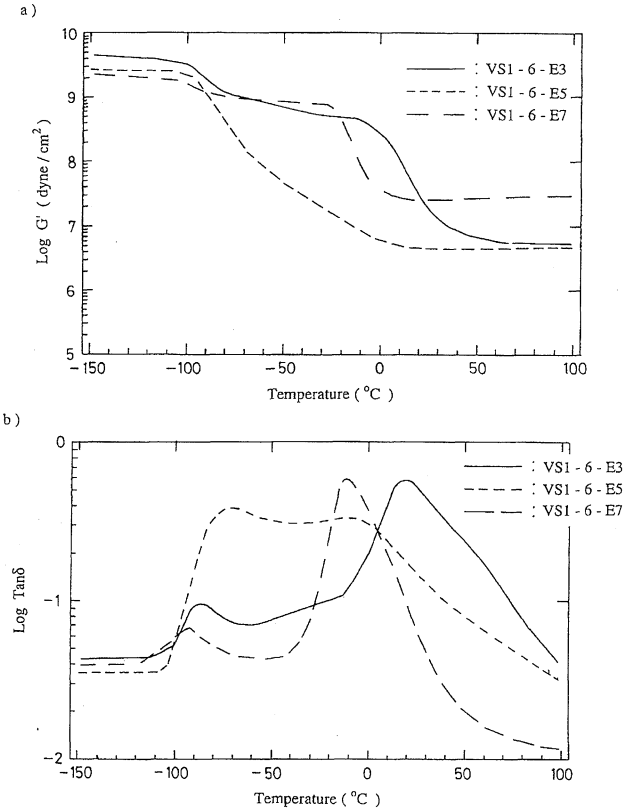


Fig. 5. Temperature dependence of G' (a) and tan δ (b) for VS1-6 series.

nents due to their lower molecular mass, while the PDMS components with $M_n = 2800$ are well separated from the PEO components. Similar results for the effects of the molecular mass of component polymer on T_g were reported for graft copolymers[21] and IPN's[22] having PDMS as a component.

It is also seen in Table 5 that T_g's for PEO component in the copolymeric networks are higher as the molecular mass of PEO component is lower, independently of the molecular mass of PDMS component. This is interpreted as the result of the decrease in the mobility of PEO chains caused by the introduction of crosslinks into both the ends, which is more enhanced as the molecular mass of PEO chains is lower.[9]

As can be seen in Figs. 4 and 5, the height of the plateau zone of G' in the T region between the T_g's of PDMS and PEO phases increases with the increase in PEO content for the copolymeric networks. In this plateau zone, the PEO phases are in the glassy state, which enhances G' for the copolymeric networks.

In the plateau zone in the T region higher than T_g of PEO, G' values for the copolymeric networks are higher than the one for the PDMS network (ca. 2×10^6 dyne cm^{-2}). This results from the microphase-separated structures in which the PEO phases act as filler in the PDMS matrix.

Swelling Behavior. Table 6 shows the degree of swelling (Q) for each sample in three kinds of solvent at room temperature. Q is defined as the ratio of the weight in swollen state to the one in dry state. THF is a good solvent for both PDMS and PEO, and cyclohaxane is a good solvent

Table 6. Degree of Swelling (Q) in THF, Cyclohexane, and Water for Each Sample

Sample	PEO content	Q		
	wt%	THF	Cyclohexane	Water
HS1-4-E3	28	3.0	1.8	1.1
HS1-4-E5	38	3.8	2.2	1.5
HS1-4-E7	41	3.2	1.7	1.5
HS1-6-E3	35	3.3	1.7	1.5
HS1-6-E5	48	3.4	1.4	2.0
HS1-6-E7	55	4.1	1.4	2.0
HS2-6-E5	33	3.2	2.0	1.6
VS1-6-E3	35	4.4	2.0	1.2
HS1-6-S1	0	5.7	6.0	1.0
GE7	87	4.1	1.0	5.6

for PDMS and a poor one for PEO, and water is a poor solvent for PDMS and a good one for PEO. This is well demonstrated by the results that the PDMS gel HS1-6-S1 and the PEO gel GE7 showed no swelling against water and cyclohexane, respectively. On the other hand, it is found that the copolymeric gels exhibit a finite swelling in both water and cyclohexane, which clearly indicates that they have an amphiphilic character. For copolymeric gels, the achievements of the amphiphilic properties have been reported for PEO/polybutadiene[14] and 2-(dimethylamino)ethyl methacrylate/polyisobutylene[15] systems.

It is well-known that the degree of swelling of polymer networks increases with the increase in chain length between neighboring crosslinking points. It should be noted that this concept is applicable to polymer networks with homogeneous structure. For polymer networks with heterogeous structures such as copolymeric networks with microphase separated morphology, dependence of Q on length of network chain may be complicated. The value of Q of HS2-6-E5 in THF is not larger than those of HS1 series, which is contrary to the general concept. This is due to the heterogeneous structures of copolymeric gels swollen in THF which are composed of the expanded PDMS chains and the aggregated PEO chains. The complicated dependence of Q on length of network chains was also reported in PEO/polybutadiene copolymeric network system.[14]

Figure 6 indicates Q in various solvents for the copolymeric gel HS1-6-E5 and the PDMS gel HS1-6-S1. The horizontal axis shows the solubility parameter (δ) of swelling solvent. As is expected, Q for HS1-6-S1 exhibits the monotonous decrease with the increase in δ, which is accompanied by the sharp decrease around δ corresponding to the theta solvent. The value of δ for ethyl methyl ketone, which is a theta solvent for PDMS around room temperature,[23] is 9.3 cal$^{1/2}$ cm$^{-3/2}$. On the other hand, for HS1-6-E5, the dependence of Q on δ shows the maximum around $\delta = 10$. This maximum should originate from the facts that both PDMS and PEO constituents have modest affinity against the solvents with δ around the maximum.

Figure 7 shows the dependence of Q on the composition of the mixtures of toluene and methanol for HS1-6-E5. The

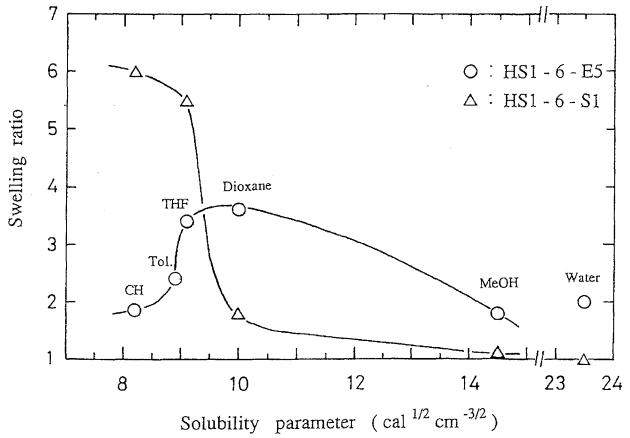


Fig. 6. Degree of swelling (Q) of HS1-6-E5 and HS1-6-S1 in various solvents. The quantity at horizontal axis is the solubility parameter (δ) of the swelling solvents.

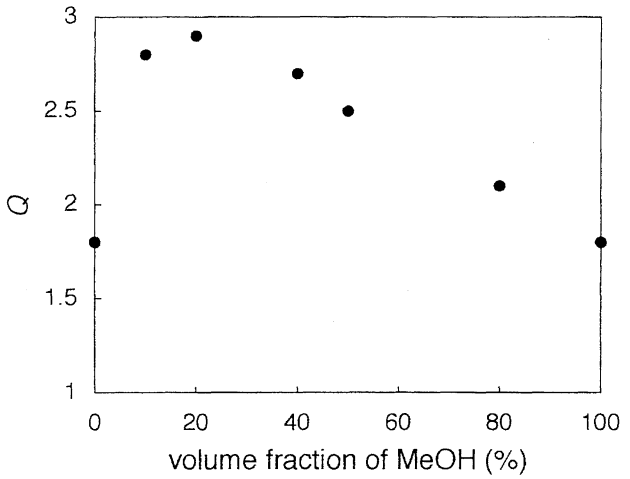


Fig. 7. Degree of swelling (Q) of HS1-6-E5 in a mixture of toluene and methanol.

change in the composition of the mixtures corresponds to the one in δ ranging from 8.9 (for toluene) to 14.5 (for methanol). As can be seen in the figure, the maximum is observed around 20 vol% of methanol. The value of δ for the mixture with 20 vol% methanol is evaluated to 9.9 $cal^{1/2}\,cm^{-3/2}$ by assuming the additivity for δ. This value is close to the δ at the maximum of Q in Fig. 6.

Figure 8 indicates the dependence of the reduced Q for water and cyclohexane on PEO content in the copolymeric networks. Since Q depends on crosslinking density, the values of Q are normalized by the one in THF for each sample in order to discuss exclusively the effects of PEO content on Q. It is found that with the increase of hydrophilic PEO content, the reduced Q for water increase and the one for cyclohexane decreases, though the reduced Q at 55 wt% PEO content is smaller than the one at 48 wt% PEO content. Since the absolute values of Q for cyclohexane and water for the network with 55 wt% PEO content are the same as those for the one with 48 wt% PEO content, as shown in Table 6, the difference in the reduced Q is caused by the difference in Q for THF as the reference. Accordingly, the inverse in the

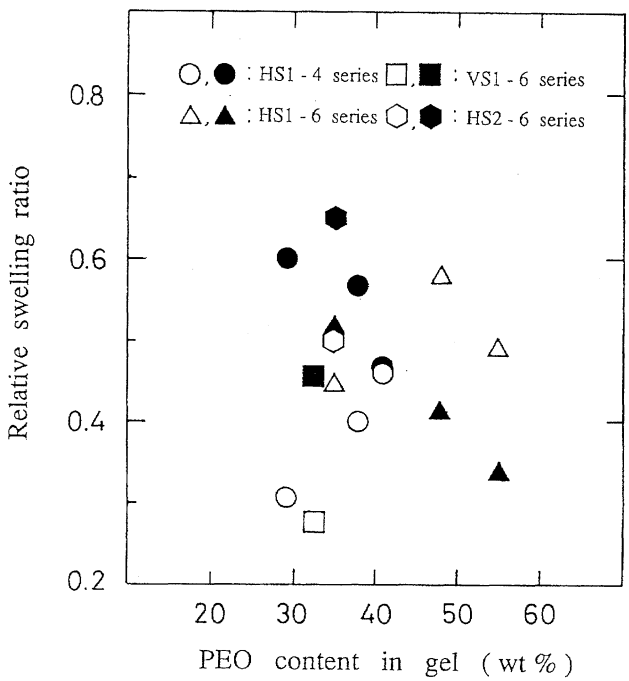


Fig. 8. Relationships between PEO content in copolymeric gels and reduced degree of swelling. Open and closed symbols represent the data for water and cyclohexane, respectively. The degrees of swelling in water and cyclohexane are reduced by the one in tetrahydrofuran.

PEO content dependence of the reduced Q around 50 wt% PEO content is only apparent. It is also found in the figure that the superiority in the magnitude of the reduced Q for water and cyclohexane is reversed around the PEO content 40 wt% which corresponds to ca. 50 mol%, i.e., intermediate composition. This result suggests that the hydrophobic and hydrophilic characters of the copolymeric networks in this study are quantitatively balanced around the intermediate composition, from the viewpoint of the degree of swelling.

Ionic Conductivity. Table 7 shows the quantity of incorporated $LiClO_4$ and T_g of PEO phase for the copolymeric networks into which $LiClO_4$ is doped. It is found that T_g of PEO phase is enhanced with the increase in the incorporated $LiClO_4$.

Figure 9 indicates the Arrhenius plots for the T dependence of conductivity (σ) for the $LiClO_4$-doped copolymeric networks. The σ increased with the rise of T, and σ around room temperature is of the order of 10^{-6} S cm^{-1}. The con-

Table 7. Quantity of $LiClO_4$ Doped into Copolymeric Gels, Glass Transition Temperature (T_g) of PEO Phase, and WLF Parameters (C_1 and C_2) of Ion Conductive Copolymeric Gels

Sample	[Li]/[O] (mol%)	T_g of PEO (°C)	C_1	C_2
HS1-6-E5-1	2.6	−23.4	11.1	44.0
HS1-6-E5-2	4.9	−4.3	6.91	68.2
HS1-6-E7	15.8	−43.2	14.0	149
HS2-6-E7-1	15.2	−38.3	13.7	46.5
HS2-6-E7-2	25.2	−33.3	16.9	37.5

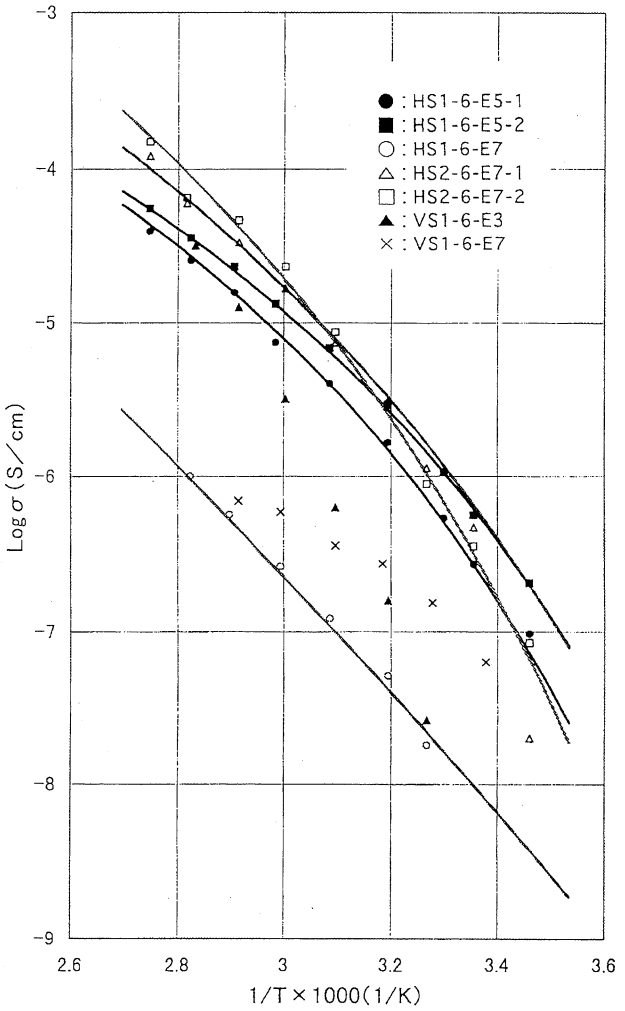


Fig. 9. Arrhenius plots for the temperature (T) dependence of conductivity (σ) for copolymeric gels. The lines represent the results of the fitting of WLF equation (Eq. 1) to the experimental data. The applications of WLF equation to the data for VS1-6-E3 and VS1-6-E7 failed because T_g's for the samples were not definitely determined due to the broad transition.

ductivity suggests that lithium cation migrates through the matrix composed of PDMS and PEO network chains. Since PDMS segments do not dissolve the cation, some PEO domains seem to form continuous phases, or some PDMS domains separating the neighboring PEO domains are so thin that the ion can penetrate through the PDMS phase by a certain hopping mechanism. Anyway, this again shows a characteristic of the amphiphilic nature of the copolymeric gels. The Arrhenius relations between σ and $1/T$ for all the samples show convexity, instead of linearity. The following William–Landel–Ferry (WLF) equation[22] based on the free volume concept was satisfactorily fitted to the experimental T dependence of σ.

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}. \quad (1)$$

It is well accepted that the WLF type of T dependence of σ means that the amorphous phase acts as the matrix carrier for the metal ions, and the free volume in the amorphous phase is important for the diffusion for the carrier.[25,26] The values of the parameters C_1 and C_2 used for fitting Eq. 1 to the experimental data are listed in Table 7. We could not apply the WLF equation to the experimental data for VS1-6-E3 and VS1-6-E7, since T_g of Li-doped VS1-6-E3 and VS1-6-E7 could not be definitely determined from DSC curves due to broad transition. In the systems in this study, the ionic mobility is considered to be governed by the free volume in polymer matrix in which the carrier ions diffuse with the segmental mobility of polymer chains in amorphous phase composed of both PDMS and PEO segments.

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