Diffusion and solution of gases in substituted polyacetylene membranes

Toshio Masuda, Yuichiro Iguchi, Ben-Zhong Tang and Toshinobu Higashimura

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan

(Received 13 January 1988; revised 17 March 1988; accepted 9 April 1988)

The coefficients of permeability, diffusion and solubility (P, D and S, respectively) of various substituted polyacetylenes for six gases (He, H_2, O_2, N_2, CO_2 and CH_4) at 25°C were determined. The polyacetylenes with a bulky substituent such as poly[1-(trimethylsilyl)-1-propyne] (poly(TMSP)) generally exhibited large P values. The especially large P values ($\sim 2 \times 10^3$–2×10^4 barrer) of poly(TMSP) were found to be based on both its D and S values being large. The polyacetylenes with a long *n*-alkyl group showed fairly large D values, while those with a phenyl group had relatively large S values. The activation parameters for P, D and S (E_P, E_D and ΔH_S, respectively) were obtained from their temperature dependences (30–70°C). The E_P values of poly(TMSP) were all negative (-9.7 to -0.4 kJ mol^{-1}). This stemmed from its small E_D values compared with those of other polymers.

(Keywords: gas permeability; diffusion; solution; poly[1-(trimethylsilyl)-1-propyne]; substituted polyacetylene; membrane)

INTRODUCTION

Poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)], a silicon-containing di-substituted acetylene polymer, exhibits extremely high gas permeability[1–4]. The permeability coefficient (P) of this polymer for oxygen reaches ~ 10 times the value for poly(dimethylsiloxane), which was previously known to have the largest P value among all the existing polymers. Properties of poly(TMSP), however, are very different from those of poly(dimethylsiloxane). For instance, poly(TMSP) is glassy at room temperature, can afford a thin tough film, and undergoes a decrease of its P_{O_2} to a value smaller than one tenth of the original value after a long period of time.

Thus far we have synthesized various, new, high molecular weight polymers from substituted acetylenes by use of catalysts based on groups 5 and 6 transition metals (Nb, Ta, Mo and W)[5]. Many of the polymers are totally soluble in low polarity solvents, film-forming, amorphous, and glassy at room temperature. Among them, polymers with a bulky substituent such as poly(TMSP) assume a sparse aggregation state, and hence exhibit high gas permeability[2,5].

One of the methods for clarifying the mechanism of gas permeation through a membrane is to examine the diffusion coefficient (D) and solubility coefficient (S). Since P can be represented by their product ($D \times S$), a detailed discussion of gas permeability is possible in terms of D and S. It is, however, known that the dual-sorption mechanism sometimes predominates gas permeation in glassy polymers[6–8]. Therefore, it must be kept in mind that discussion of D and S for glassy polymers is tentative to some extent. Even if this is taken into account, the evaluation of D and S of poly(TMSP) and other polyacetylenes seems very important to elucidate their gas permeation mechanism.

The present paper describes the gas permeation behaviour of various substituted polyacetylenes with emphasis on their D and S values. It has been revealed that polyacetylenes with a bulky substituent such as poly(TMSP) are highly gas permeable, which is attributable to both their D and S values being large. Their activation parameters are also discussed.

EXPERIMENTAL

Polymer synthesis

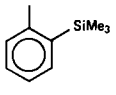
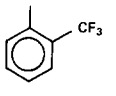
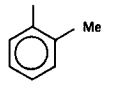
Table 1 lists the types of polymer sample, the polymerization catalysts, and their weight average molecular weights ($\bar{M}_w$) and dispersity ratios ($\bar{M}_w/\bar{M}_n$). These polymer samples were prepared according to the methods of the references shown in *Table 1*. The polymerizations were carried out under dry nitrogen by use of Erlenmeyer flasks, each equipped with a three-way stopcock, and hypodermic syringes. The polymers formed were recovered by precipitation into methanol. The yields of the polymers were usually $>70\%$. The $\bar{M}_w$ values of the polymers were in a range of $\sim 2 \times 10^5$–2×10^6, being quite high, and their $\bar{M}_w/\bar{M}_n$ ratios were within the range $\sim$2–4.

Membrane preparation

All the membranes were obtained by casting polymers from toluene solutions (2–5%). Polymer solutions were cast into a flat-bottomed Petri dish to prepare the thicker membranes (thickness 100–500 μm), whereas they were cast on a glass plate and extended with a doctor knife to prepare the thinner ones (thickness 10–100 μm). The solvent was evaporated slowly at room temperature over a few days to give homogeneous membranes with uniform thickness, and finally the solvent was removed as completely as possible by keeping the membranes in a vacuum drying oven at room temperature for a few days. The membrane thickness was chosen according to the gas permeability of the polymer. For example, for poly(TMSP), which is the most gas-permeable, a membrane as thick as 500 μm was prepared from 2%

0032-3861/88/112041-09$03.00

Table 1 Preparation of substituted polyacetylenes

R	$+CR=CR'+_n$ R'	Catalyst	Method[a]	$\bar{M}_w$[b] / 10^3	$\bar{M}_w$[b] / $\bar{M}_n$	Ref.
Me	$SiMe_3$	$TaCl_5$	A	1300	2.2	1
Me	$SiMe_2CH_2SiMe_3$	$TaCl_5$	A	690	2.3	9
Me	$SiMe_2CH_2CH_2SiMe_3$	$TaCl_5$-Ph_4Sn	A	150	1.9	9
Me	$SiMe_2$-*n*-C_6H_{13}	$TaCl_5$-Ph_3Bi	A	560	1.8	10
Me	*n*-C_7H_{15}	$MoCl_5$-Ph_4Sn	B	500	2.4	5
Ph	Me	$TaCl_5$-*n*-Bu_4Sn	A	1500	2.5	5
Ph	Et	$NbCl_5$-*n*-Bu_4Sn	A	860	2.3	11
Ph	*n*-C_6H_{13}	$NbCl_5$-*n*-Bu_4Sn	A	630	2.4	11
Cl	*n*-C_8H_{17}	$MoCl_5$-*n*-Bu_4Sn	B	500	2.2	12
Cl	*n*-C_6H_{13}	$MoCl_5$-*n*-Bu_4Sn	B	550	2.5	12
Cl	*n*-C_4H_9	$MoCl_5$-*n*-Bu_4Sn	B	450	2.0	12
Cl	Ph	$Mo(CO)_6$-CCl_4-hν	C	430	1.9	5
H	CH(*n*-C_5H_{11})$SiMe_3$	$MoCl_5$-Et_3SiH	D	450	2.1	13
H	CH(*n*-C_3H_7)$SiMe_2$-*n*-C_6H_{13}	$MoCl_5$-Ph_3Sb	D	410	2.0	13
H	CH(*n*-C_3H_7)$SiMe_2Ph$	WCl_6-Ph_3Sb	D	210	2.5	13
H	*t*-Bu	$MoCl_5$	B	660	2.0	5
H		$MoCl_5$-Ph_3SiH	B	1900	3.8	14
H		WCl_6-Ph_4Sn	B	1500	3.9	15
H		$W(CO)_6$-CCl_4-hν	C	260	3.9	16

[a] Polymerization conditions for A are: in toluene, 80°C, 24 h, $[M]_0 = 0.50$–$1.0\,mol\,l^{-1}$, $[Cat] = 10$–$30\,mmol\,l^{-1}$. Conditions B–D are modified as follows: B, 30°C; C, in CCl_4, 30°C; D, 0°C

[b] Determined by gel permeation chromatography on the basis of a polystyrene calibration

toluene solution. On the other hand, with poly(1-chloro-2-phenylacetylene), which is one of the least permeable polyacetylenes, membranes ~20 μm thick (for CH_4 and N_2) and ~200 μm (for other gases) were prepared from 3% solution. Membrane thicknesses were measured with a micrometer.

It has been reported that the P_{O_2} value of a poly(TMSP) membrane (thickness 260 μm) decreased with time when the membrane was stored in vacuum at room temperature[3]. However, the value of a poly(TMSP) membrane (thickness 500 μm) in the present study hardly decreased even after 2 weeks in air at room temperature. By way of precaution, the measurements using the poly(TMSP) membrane were carried out within a few days of membrane preparation in the present work.

Measurement of gas permeabilities

The gas permeation was observed on a K-315-N gas permeability apparatus (Rikaseiki Co., Japan) equipped with a MKS Baratron detector. High purity gases (He, H_2, O_2, N_2, CO_2 and CH_4; purities all >99.5%; Teisan K. K., Japan) were used. The measuring temperature was 25°C unless otherwise specified. The downstream side of the membrane (7.0 cm^2 disc) was evacuated to about 0.1 mmHg (~13 Pa), the upstream side was filled with the gas at about 1 atm (10^5 Pa), and the increase of pressure in a downstream receiving vessel was measured. For very quick permeation, a spare receiving vessel (the volume is 4.3 times as large) was also used.

The P values were calculated from the slopes of time–pressure curves in the steady state where Fick's law held. The D values were determined by the time lag method using the following equation:

$$D = l^2/6\theta$$

Here, l is the membrane thickness, and θ is the time lag, which is given by the intercept of the asymptotic line of the time–pressure curve to the time axis. The membrane thickness was controlled so that the time lag would be in the range 10–300 s, preferably 30–150 s. When the time lag was <10 s, the error of measurement became relatively large. If the time lag was, on the contrary, >300 s, the error based on the baseline drift became serious. The S values were calculated by using equation $S \equiv P/D$.

Activation energies for permeability (E_P) were determined by least-squares treatment of the Arrhenius plot of the P values measured at 30, 40, 50, 60 and 70°C. Activation energies for diffusion (E_D) were similarly obtained from the Arrhenius plot of the D values. Heats of solution (ΔH_S) were calculated as the difference, $E_P - E_D$.

RESULTS AND DISCUSSION

The abbreviations used in the figures for conventional polymers are as follows: PDMS, poly(dimethylsiloxane), P4M1P, poly(4-methyl-1-pentene); NR, natural rubber; PPO, poly[*p*-(2,6-dimethyl)phenylene oxide]; EtCe, ethyl cellulose; PTFE, poly(tetrafluoroethylene); LDPE, low density polyethylene; PSt, polystyrene; PVC, poly(vinyl chloride); PDMBD, poly(dimethylbutadiene); PET(A), amorphous poly(ethylene terephthalate).

Table 2 Gas permeability coefficients (P) of substituted polyacetylenes[a]

No.	R	R′	P (barrer[b]) He	H_2	O_2	N_2	CO_2	CH_4
With bulky substituent								
1	Me	$SiMe_3$	2200	5200	3000	1800	19000	4300
2	H	*t*-Bu	180	300	130	43	560	85
3	Me	$SiMe_2CH_2SiMe_3$	180	270	75	21	310	45
4	Me	$SiMe_2CH_2CH_2SiMe_3$	130	180	50	14	150	28
5	H		170	290	78	24	290	38
6	H		130	140	25	7.3	130	6.6
With long n-alkyl group								
7	Me	*n*-C_7H_{15}	48	76	35	14	130	40
8	Cl	*n*-C_8H_{17}	43	76	47	16	170	46
9	Cl	*n*-C_6H_{13}	41	66	32	11	130	33
10	Cl	*n*-C_4H_9	59	100	35	10	180	30
11	Me	$SiMe_2$-*n*-C_6H_{13}	31	53	18	4.3	71	13
12	H	$CH(n\text{-}C_5H_{11})SiMe_3$	60	84	27	8.7	120	21
13	H	$CH(n\text{-}C_3H_7)SiMe_2$-*n*-$C_6H_{13}$	58	42	19	6.3	70	17
With phenyl group								
14	Ph	Me	30	43	6.3	2.2	25	2.8
15	Ph	Et	40	57	12	4.5	40	4.4
16	Ph	*n*-C_6H_{13}	30	45	14	5.5	48	14
17	Ph	Cl	23	29	5.1	1.0	23	1.3
18	H		29	39	8.1	3.0	15	3.0
19	H	$CH(n\text{-}C_3H_7)SiMe_2Ph$	25	29	9.5	2.5	54	7.0

[a] P values measured at 25°C
[b] 1 barrer = 1×10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}

Permeability and permselectivity

First, the P values of various substituted polyacetylenes for six kinds of gases were measured at 25°C (*Table 2*). The polyacetylenes have been grouped in *Table 2* according to both the kind of substituents and their gas permeation behaviour. All the polyacetylenes of the first group possess a bulky (globular) substituent. Typical of such bulky groups is the trimethylsilyl group. The polyacetylenes of the second group are distinguished by the presence of a long *n*-alkyl group. The third type of polyacetylene generally has a phenyl group. When a polyacetylene has two different types of substituent, this grouping is somewhat equivocal. In such a case, the polymer has been classified according to its gas permeation behaviour.

Interestingly, the polyacetylenes of the first group (with a bulky substituent) generally exhibited large P values for every gas (*Table 2*). The values for poly(TMSP) are outstanding, as has already been observed in the literature[1-4]. The fact that poly(*tert*-butylacetylene) and poly[*o*-(trifluoromethyl)phenylacetylene] are also very permeable indicates that the presence of a silyl group is not a requirement for high gas permeability.

The P values for the polyacetylenes of the second group (with a long *n*-alkyl group) were medium in magnitude. This means that long *n*-alkyl groups do not necessarily favour the gas permeability of substituted polyacetylenes. It contrasts with the case of rubbery α-olefin-SO_2 copolymers[17] where the P_{O_2} value increases with increasing alkyl chain length.

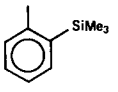
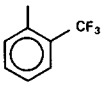
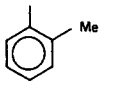
The polyacetylenes of the third group (with a phenyl group) showed rather small P values. This suggests that phenyl groups stack on one another, which gives rise to a polymer morphology giving low gas permeability. The small P values of poly(1-chloro-2-phenylacetylene) have already been noted[2].

While poly(TMSP) is highly permeable to every gas, its selectivity for the permeation of two different gases (permselectivity) is not high. This should be associated with its sparse molecular aggregation state. In general, a tendency is often seen that the lower the permeability of a polymer, the higher the permselectivity of the polymer. This also seems roughly to hold with substituted polyacetylenes; for instance, polyacetylenes with a phenyl group usually show low permeability but high permselectivity among substituted polyacetylenes. It is noted that although poly[*o*-(trifluoromethyl)phenylacetylene] is fairly permeable to gases, its P_{CO_2}/P_{CH_4} and P_{O_2}/P_{N_2} ratios are quite large.

Diffusion coefficient

Table 3 lists the diffusion coefficients (D) of substituted polyacetylenes for various gases. Obviously, poly(TMSP) has larger D values than any other polyacetylene for all the gases in *Table 3*. The D values of poly(TMSP) agree fairly well with the values for O_2, N_2, CO_2 and CH_4

Table 3 Gas diffusion coefficients (D) of substituted polyacetylenes[a]

No.	R	R'	$10^7 D$ ($cm^2 s^{-1}$)					
			He	H_2	O_2	N_2	CO_2	CH_4
With bulky substituent								
1	Me	$SiMe_3$	1100	1800	220	150	250	160
2	H	*t*-Bu	520	340	37	19	34	14
3	Me	$SiMe_2CH_2SiMe_3$	480	320	14	5.8	7.4	3.1
4	Me	$SiMe_2CH_2CH_2SiMe_3$	320	210	17	7.3	14	4.8
5	H		210	120	9.8	3.5	6.9	2.6
6	H		280	79	4.0	1.0	1.9	0.43
With long n-*alkyl group*								
7	Me	n-C_7H_{15}	80	110	32	13	31	17
8	Cl	n-C_8H_{17}	270	160	80	18	18	11
9	Cl	n-C_6H_{13}	320	160	23	14	14	9.9
10	Cl	n-C_4H_9	270	100	12	6.0	7.0	3.4
11	Me	$SiMe_2$-n-C_6H_{13}	220	100	9.4	7.8	6.3	3.2
12	H	$CH(n\text{-}C_5H_{11})SiMe_3$	250	110	11	4.9	5.2	3.3
13	H	$CH(n\text{-}C_3H_7)SiMe_2$-$n$-$C_6H_{13}$	140	280	15	9.2	9.9	5.3
With phenyl group								
14	Ph	Me	44	45	1.3	0.76	1.0	0.41
15	Ph	Et	49	43	3.4	1.3	3.3	0.34
16	Ph	n-C_6H_{13}	49	46	8.6	1.5	8.2	2.5
17	Ph	Cl	22	22	2.2	0.72	1.7	0.14
18	H		110	33	1.6	0.75	0.50	0.30
19	H	$CH(n\text{-}C_3H_7)SiMe_2Ph$	89	37	3.0	1.3	1.5	0.70

[a] D values measured at 25°C by the 'time lag' method

reported recently[4]. Broadly speaking, the D values of the polyacetylenes with a long n-alkyl group are close in magnitude to the values of those with a bulky substituent, except for poly(TMSP). On the other hand, the D values of the polyacetylenes with a phenyl group are much smaller than the values of those with a bulky substituent.

A tendency has generally been observed that D values decrease with increasing molecular diameter of gas[18]. So the dependence of D value on molecular diameter of gas was examined for substituted polyacetylenes. Good linear relationships held in the log–log plot of the D value of substituted polyacetylenes *versus* the molecular diameter of gases. *Figure 1* shows plots for the three kinds of polyacetylene and two conventional polymers (the following molecular diameters from reference 19 were used: H_2, 2.60; He, 2.66; O_2, 2.93; N_2, 3.13; CO_2, 3.23; CH_4, 3.24 Å; 1 Å = 10^{-1} nm).

As seen from *Figure 1*, the D value decreases with increasing molecular diameter of gas for all the polymers. The dependence of the D value on the molecular diameter of gases is the greatest in poly(1-phenyl-1-propyne). Concerning the substituent effect of polyacetylenes, the D value for every gas decreases in the following order: poly(TMSP) > poly(2-decyne) > poly(1-phenyl-1-propyne). The large D values of poly(TMSP) might be due partly to the presence of molecular-scale voids in the polymer. In contrast, the large D value of

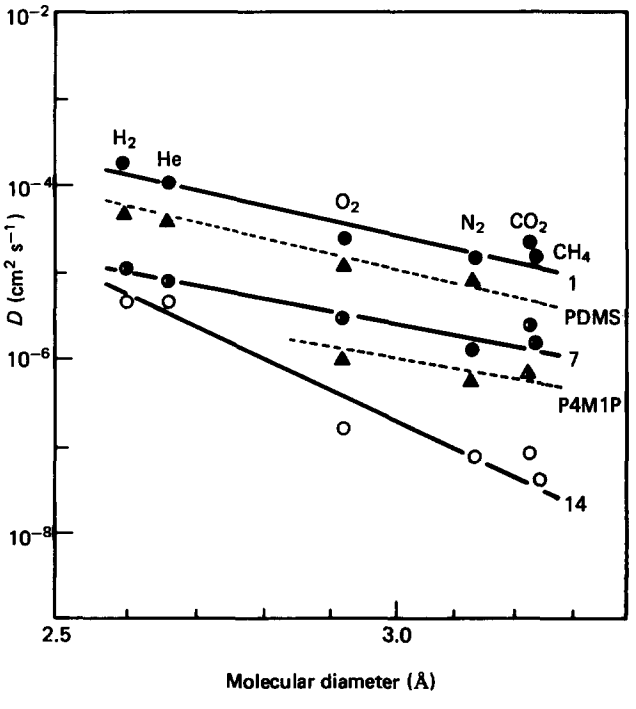
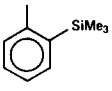
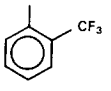
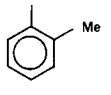


Figure 1 Relationship between the molecular diameter of gases and the diffusion coefficient (D) of typical polyacetylenes and two conventional polymers (D at 25°C; numbers correspond to polyacetylene numbers in *Tables 2–4*; data for conventional polymers from Reference 18)

Table 4 Gas solubility coefficients (S) of substituted polyacetylenes[a]

No.	R	R'	10^3S (cm^3 (STP) cm^{-3} $cmHg^{-1}$)					
		$-(CR=CR')_n-$	He	H_2	O_2	N_2	CO_2	CH_4
With bulky substituent								
1	Me	$SiMe_3$	2.0	2.9	14	12	76	27
2	H	*t*-Bu	0.35	0.88	3.5	2.3	16	6.1
3	Me	$SiMe_2CH_2SiMe_3$	0.38	0.84	5.4	3.6	42	15
4	Me	$SiMe_2CH_2CH_2SiMe_3$	0.41	0.86	2.9	1.9	11	5.8
5	H		0.81	2.4	8.0	6.9	42	15
6	H		0.46	1.8	6.3	7.3	68	15
With long n-alkyl group								
7	Me	n-C_7H_{15}	0.60	0.69	1.1	1.1	4.2	2.4
8	Cl	n-C_8H_{17}	0.16	0.48	0.59	0.89	9.4	4.2
9	Cl	n-C_6H_{13}	0.13	0.41	1.4	0.79	9.3	3.3
10	Cl	n-C_4H_9	0.22	1.0	2.9	1.7	26	8.8
11	Me	$SiMe_2$-n-C_6H_{13}	0.14	0.53	1.9	0.55	11	4.1
12	H	$CH(n\text{-}C_5H_{11})SiMe_3$	0.24	0.76	2.5	1.8	23	6.4
13	H	$CH(n\text{-}C_3H_7)SiMe_2$-$n$-$C_6H_{13}$	0.41	0.15	1.3	0.68	7.1	3.2
With phenyl group								
14	Ph	Me	0.68	0.96	4.8	2.9	25	6.8
15	Ph	Et	0.82	1.3	3.5	3.5	12	13
16	Ph	n-C_6H_{13}	0.61	0.98	1.6	3.7	5.9	5.6
17	Ph	Cl	1.0	1.3	2.3	1.4	14	9.3
18	H		0.26	1.2	5.1	4.0	30	10
19	H	$CH(n\text{-}C_3H_7)SiMe_2Ph$	0.28	0.78	3.2	1.9	36	10

[a] S values calculated as quotients, P/D (P, D in *Tables 2* and *3*)

poly(2-decyne) is likely to be due to the flexibility and mobility of the side *n*-alkyl group. It is noted that the curve for poly(dimethylsiloxane) is close to that for poly(TMSP), while the curve for poly(4-methyl-1-pentyne) is near that for poly(2-decyne). This may be explained in terms of the similarity in their structure.

Solubility coefficient

The solubility coefficients (S) of substituted polyacetylenes for various gases are given in *Table 4*. Poly(TMSP) clearly shows the largest S values for every gas. Unlike the D values, the S values of the polyacetylenes with a phenyl group resemble the values of those with a bulky substituent, while the S values of polyacetylenes with a long *n*-alkyl group are somewhat smaller.

A good linear relationship has been observed between S values for natural rubber and the boiling points of gases[20]. *Figure 2* gives the relationship between the log S for several polyacetylenes as well as conventional polymers and the boiling points of gases (the following boiling points from reference 21 were used: He, 4.25; H_2, 20.35; N_2, 77.35; O_2, 90.15; CH_4, 109.15; CO_2, 194.65 K). As the boiling point of gas increases, the S value increases not only for poly(dimethylsiloxane) and poly(4-methyl-1-pentene) but also for the three polyacetylenes. Interestingly, the S value of poly(TMSP) is larger than the values of any other polymers for every

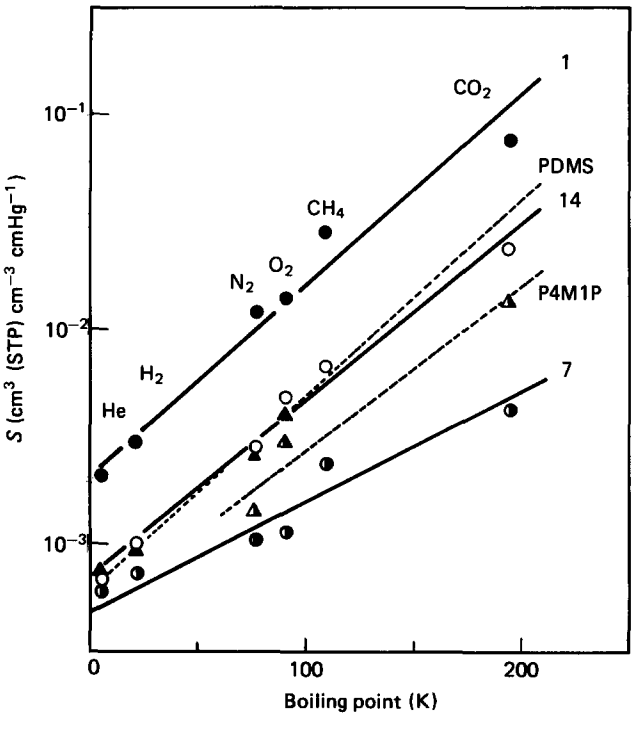


Figure 2 Relationship between the boiling point of gases and the solubility coefficient (S) of typical polyacetylenes and two conventional polymers (S at 25°C; numbers correspond to polyacetylene numbers in *Tables 2–3*; data for conventional polymers from Reference 18)

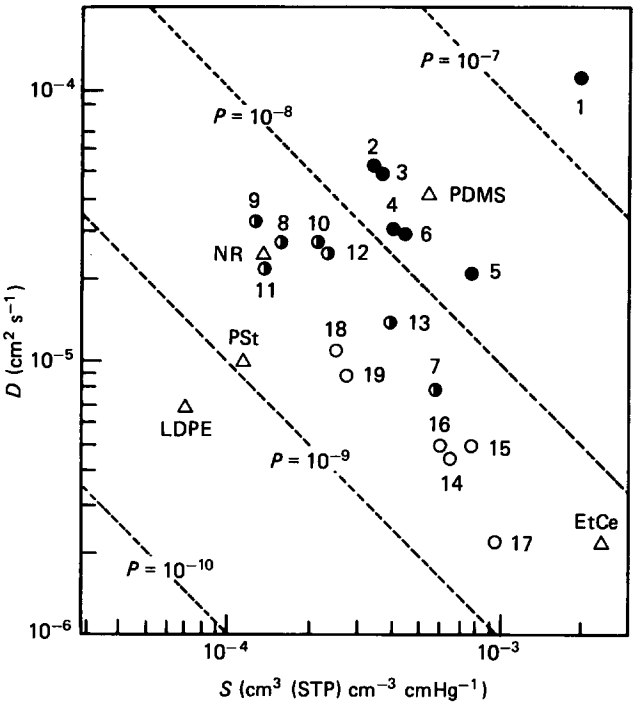


Figure 3 Plot of diffusion coefficient (D) *versus* solubility coefficient (S) of various polyacetylenes and several conventional polymers for helium (25°C; the numbers correspond to polyacetylene numbers in *Tables 2–4*; data for conventional polymers from References 18 and 22)

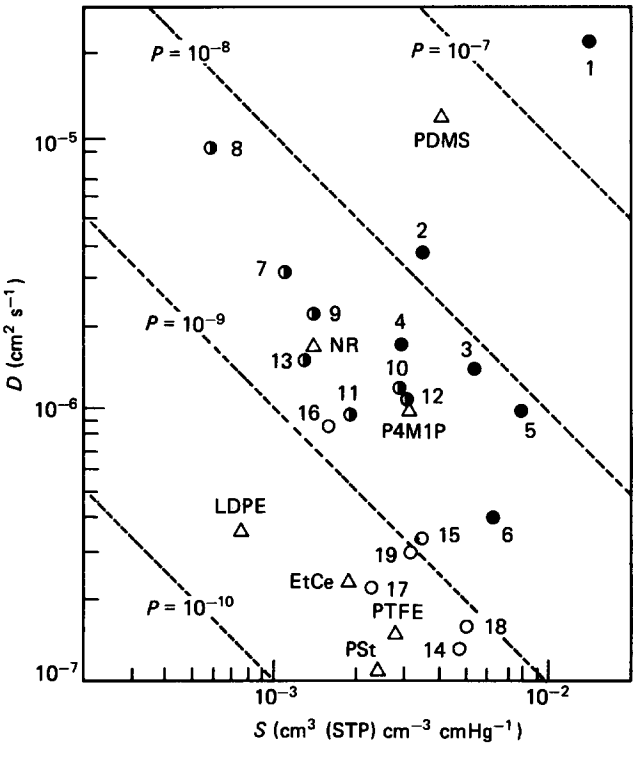


Figure 4 Plot of diffusion coefficient (D) *versus* solubility coefficient (S) of various polyacetylenes and several conventional polymers for oxygen (25°C; the numbers correspond to polyacetylene numbers in *Tables 2–4*; data for conventional polymers from References 18 and 22)

gas. Unlike the D value, the S value of poly(1-phenyl-1-propyne) is higher than that of poly(2-decyne); this might be interpreted in terms of affinity of the phenyl group for gases. It is seen in *Figure 2* that the S values of poly(dimethylsiloxane) and poly(4-methyl-1-pentene) are quite large, being near those of poly(1-phenyl-1-propyne).

Permeability as the product of D and S

Figure 3 illustrates the plot of D *versus* S for substituted polyacetylenes and He, which is a small molecule with a low boiling point. *Figure 3* also contains data for some conventional polymers. Since $P = D \times S$, the P value increases as a point goes up and to the right. The polyacetylenes with a bulky substituent (nos. 1–6; filled circles) have large D and S values, which results in large P values. The plot of the polyacetylenes with a long *n*-alkyl group (nos. 7–13; half-filled circles) is to the left of the polyacetylenes with a bulky substituent. Therefore, the finding that the P values of the polyacetylenes with a long *n*-alkyl group are smaller than the values of those with a bulky substituent is attributable to the small S values of the former polymers. In contrast, the polyacetylenes with a phenyl group (nos. 14–19; open circles) are located below those with a bulky substituent. This means that the small P values of those with a phenyl group are due to their small D values.

The D–S plot for O_2, which is larger than He and has a higher boiling point, is depicted in *Figure 4*. The polyacetylenes with a bulky substituent again exhibit large values for both diffusion and solution. The

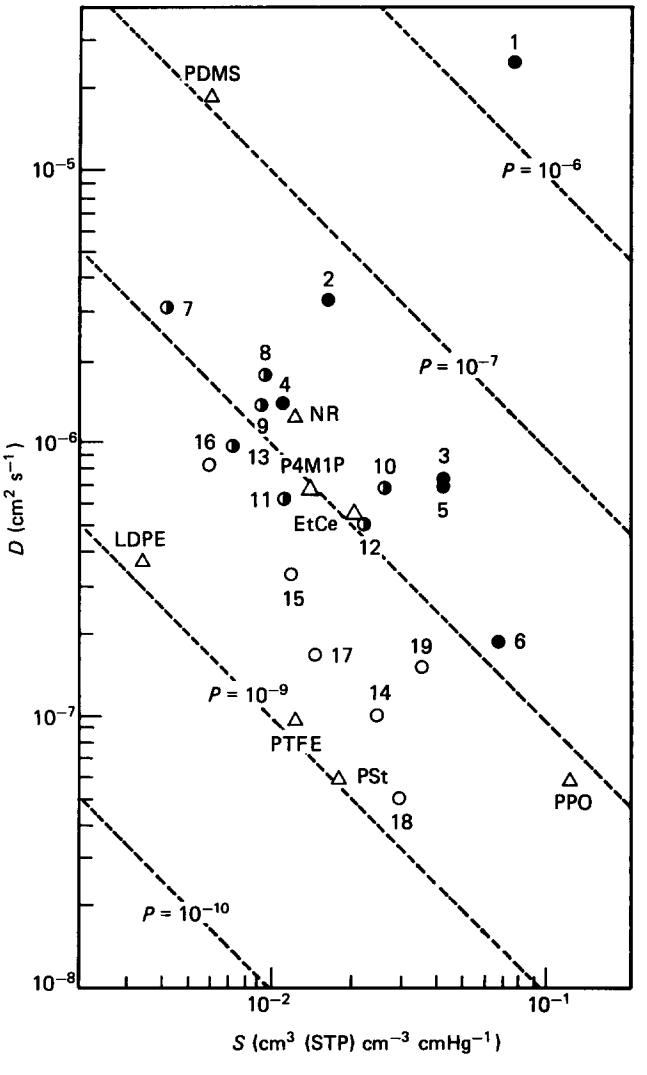
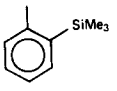
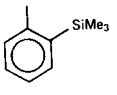
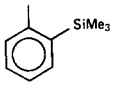


Figure 5 Plot of diffusion coefficient (D) *versus* solubility coefficient (S) of various polyacetylenes and several conventional polymers for carbon dioxide (25°C; numbers correspond to polyacetylene numbers in *Tables 2–4*; data for conventional polymers from References 18 and 22)

Table 5 Activation parameters for gas permeation through substituted polyacetylenes[a]

No.[b]	$-(CR=CR')_n-$ R	R'	Gas He	H_2	O_2	N_2	CO_2	CH_4
Activation energy for permeation, E_p (kJ mol^{-1})								
1	Me	$SiMe_3$	−0.4	−2.7	−6.7	−5.1	−9.7	−6.3
5	H		2.9	1.9	−3.9	3.8	0.7	0.4
7	Me	n-C_7H_{15}	20.2	20.0	22.3	25.8	15.1	22.9
9	Cl	n-C_6H_{13}	21.7	20.9	20.0	25.0	13.9	21.7
12	H	$CH(n\text{-}C_5H_{11})SiMe_3$	5.0	5.4	5.0	7.5	1.7	5.0
14	Ph	Me	10.1	8.1	15.8	22.3	7.5	22.8
17	Ph	Cl	15.7	13.8	15.5	24.1	6.7	28.7
Activation energy for diffusion, E_D (kJ mol^{-1})								
1	Me	$SiMe_3$	4.0	2.5	5.0	5.0	0.4	4.9
5	H		5.8	11.6	11.2	36.0	11.5	32.7
7	Me	n-C_7H_{15}	14.8	9.2	36.4	24.2	23.3	31.9
9	Cl	n-C_6H_{13}	12.6	15.6	22.6	18.4	26.7	26.8
12	H	$CH(n\text{-}C_5H_{11})SiMe_3$	8.0	4.2	8.0	12.1	13.4	12.1
14	Ph	Me	8.9	5.7	23.3	14.1	33.9	34.0
17	Ph	Cl	31.2	17.0	19.7	36.4	21.6	41.4
Heat of solution, ΔH_S (kJ mol^{-1})								
1	Me	$SiMe_3$	−4.4	−5.2	−11.7	−10.1	−10.1	−11.2
5	H		−2.9	−9.7	−15.1	−32.2	−10.8	−32.3
7	Me	n-C_7H_{15}	5.4	10.8	−14.1	1.6	−8.2	−9.0
9	Cl	n-C_6H_{13}	9.1	5.3	−2.6	6.6	−12.8	−5.1
12	H	$CH(n\text{-}C_5H_{11})SiMe_3$	−3.0	1.2	−3.0	−4.6	−11.7	−7.1
14	Ph	Me	1.2	2.4	−7.5	8.2	−26.4	−11.2
17	Ph	Cl	−15.5	−3.2	−4.2	−12.3	−14.9	−12.7

[a] E_p and E_D values determined from the P and D values measured at 30, 40, 50, 60 and 70°C; ΔH_s values calculated as differences, $E_P - E_D$
[b] Numbers correspond to those in *Tables 2–4*

polyacetylenes with a long n-alkyl group have smaller S values than those with a bulky substituent, while those with a phenyl group have smaller D values. These are the same tendencies as for He in *Figure 3*. As seen from the ordinate and abscissa of *Figures 3* and *4*, the D values for O_2 are about one order of magnitude smaller than those for He, while the S values for O_2 are about one order of magnitude larger.

Figure 5 shows the D–S plot for CO_2. It is noted that the D values for CO_2 are about one order of magnitude smaller than those for O_2, whereas the S values for CO_2 are about one order of magnitude larger (compare *Figure 5* with *Figure 4*). This is attributable to the fact that CO_2 is even larger than O_2 and has a higher boiling point. It is of great interest that the D values of substituted polyacetylenes for CO_2 vary with the kind of substituent over a wide range, by a factor of 500 (cf. a factor of 50 for He, as seen in *Figure 3*). This indicates that the diffusivity of a large molecule such as CO_2 is greatly dependent on the polymer structure. In the D–S profile for CO_2, the polyacetylenes with a long n-alkyl group are located only slightly to the left of those with a bulky substituent, while those with a phenyl group are well below them.

Of the conventional polymers considered in *Figures 3–5*, poly(dimethylsiloxane) is located near the polyacetylenes with a bulky substituent, natural rubber and poly(4-methyl-1-pentene) are close to those with a long n-alkyl group, and polystyrene and ethyl cellulose are near those with a phenyl group. Though the main chain structures of these conventional polymers are very different from those of substituted polyacetylenes, their overall structure and/or nature appear to resemble those of respective groups of polyacetylenes.

It is not immediately obvious from *Table 2* how the P value of a polymer depends on the nature of gases. However, D and S can be correlated with the molecular diameter and boiling point of gas, respectively, as shown in *Figures 1* and *2*. Therefore, P can also be expressed in terms of them. For poly(TMSP), for instance, D, S and P are formulated by the least-squares treatment, as follows:

$$\log D = -10.1 \log (\text{m.d.}) + 0.319$$

$$\log S = 0.00848 (\text{b.p.}) - 2.65$$

$$\log P = \log D \times S = -10.1 \log (\text{m.d.}) + 0.00848 (\text{b.p.}) - 2.33$$

Here m.d. is molecular diameter (Å), and b.p. is boiling point (K). The P value of poly(TMSP) for a gas not investigated can be estimated by substituting the molecular diameter and boiling point of the gas into the above equation for P. The corresponding equations could be derived for all the polyacetylenes in the present study.

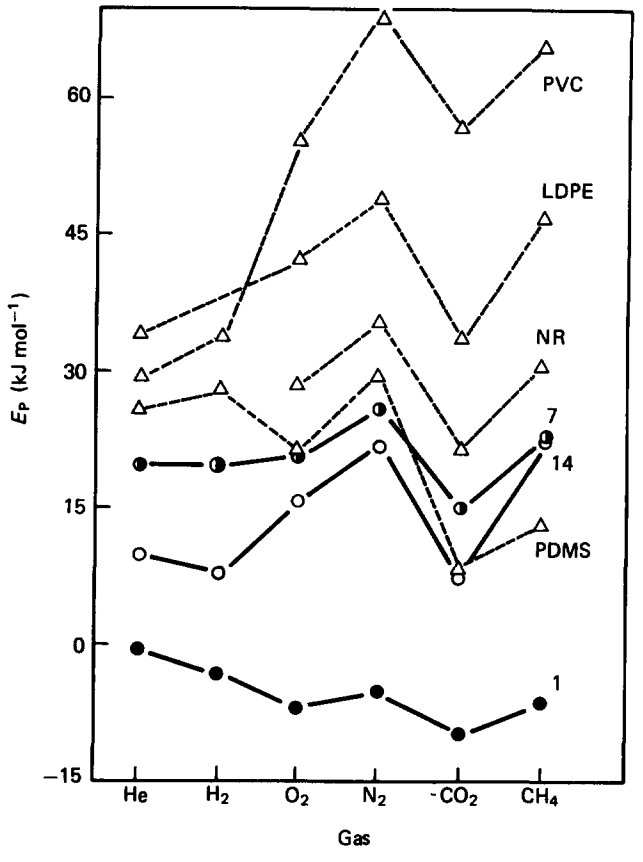


Figure 6 Activation energies for the gas permeabilities (P) of typical polyacetylenes and several conventional polymers (numbers correspond to polyacetylene numbers in *Tables 2–4*; data for conventional polymers from References 18 and 22)

Permselectivity as a function of D and S

When the equation $P = D \times S$ is assumed, P_{O_2}/P_{N_2} can be expressed as follows:

$$\frac{P_{O_2}}{P_{N_2}} = \frac{D_{O_2}}{D_{N_2}} \times \frac{S_{O_2}}{S_{N_2}}$$

The D_{O_2}/D_{N_2} value (1.03) for poly(dimethylsiloxane) is very close to unity, and its P_{O_2}/P_{N_2} value (2.04) is virtually governed by its S_{O_2}/S_{N_2} value (2.08)[23]. In contrast, the S_{O_2}/S_{N_2} values of not only poly(TMSP)[4] but also most of the substituted polyacetylenes are closer to unity than are their D_{O_2}/D_{N_2} values (see *Tables 3* and *4*). This means, interestingly, that the P_{O_2}/P_{N_2} values of the present polymers are mainly controlled by their D_{O_2}/D_{N_2} values.

The P_{CO_2}/P_{CH_4} value (3.19) for poly(dimethylsiloxane) is again governed practically only by its S_{CO_2}/S_{CH_4} value (2.94), while its D_{CO_2}/D_{CH_4} value (1.08) is very close to unity[23]. On the other hand, the contributions of D_{CO_2}/D_{CH_4} and S_{CO_2}/S_{CH_4} to P_{CO_2}/P_{CH_4} in substituted polyacetylenes are comparable (see *Tables 3* and *4*). This finding is worth noting if the fact that the sizes of CO_2 and CH_4 are similar while their natures are dissimilar is taken into consideration. Consequently it can be said that, in general, the permselectivity in substituted polyacetylenes, which are glassy at room temperature, is more affected by the difference in diffusivity than that of poly(dimethylsiloxane), which is rubbery at room temperature.

Activation parameters

Table 5 lists the activation parameters of representative polyacetylenes among the three groups. The E_P values of poly(TMSP) for the six gases were all negative; i.e. the lower the temperature, the more permeable the poly(TMSP) membrane. The negative E_P values of poly(TMSP) have been reported so far with O_2 and N_2[2] and with xenon[24]. A negative E_P value is very rare among conventional polymers except for readily condensable gases. The E_P values of the polyacetylenes in *Table 5* are in the range -10 to $+30$ kJ mol^{-1}, being negative or relatively small positive values. E_P can be divided into E_D and ΔH_S. The E_D values of the polyacetylenes are all positive, while their ΔH_S values are either negative or positive. This is consonant with the tendency of conventional polymers. Linear relationships have been observed between the E_D values of amorphous polymers and the squares of the molecular diameters of gases[25]. No such linearity, however, held with substituted polyacetylenes (see *Table 5*). It appears that the linearity applies to rubbery polymers but not to glassy polymers.

Figure 6 compares the E_P values of representative substituted polyacetylenes with those of several conventional polymers. As seen in *Figure 6*, the E_P values of poly(TMSP) are extraordinarily small compared with those of all the existing polymers. The E_P values of poly(1-phenyl-1-propyne) and poly(2-decyne) are similar to those of poly(dimethylsiloxane). Less gas permeable polymers usually have much larger E_P values.

Figure 7 depicts the E_D *versus* ΔH_S profiles of three types of polyacetylenes and several conventional polymers for O_2, for the purpose of clarifying the reason for the small E_P values of substituted polyacetylenes. Most of the ΔH_S values lie in a relatively narrow range of -20 to

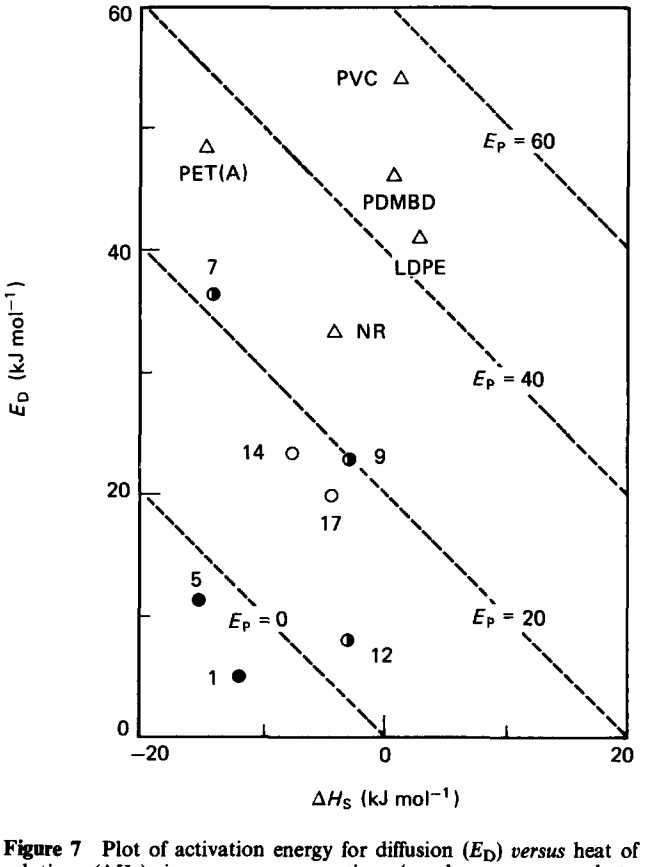


Figure 7 Plot of activation energy for diffusion (E_D) *versus* heat of solution (ΔH_S) in oxygen permeation (numbers correspond to polyacetylene numbers in *Tables 2–4*; data for conventional polymers from References 18 and 22)

0 kJ mol^{-1}, irrespective of the kind of polymer. In contrast, the E_D values are scattered over a wide range of ~ 0 to $+60$ kJ mol^{-1}. Thus, this proves that the small E_P values of polyacetylenes mainly originate from their small E_D values compared with those of conventional polymers. The small E_D values of polyacetylenes, especially that of poly(TMSP), mean that the diffusion of gases does not greatly depend on temperature. This appears to be associated with the high glass transition temperatures of polyacetylene and microvoid-containing sparse morphological structure.

ACKNOWLEDGEMENTS

We thank Professor H. Odani, Institute for Chemical Research, Kyoto University for many helpful discussions. Thanks are also due to Shin-Etsu Chemical Co. Ltd and Government Industrial Research Institute, Nagoya for the donation of 1-silyl-1-propyne and *o*-(trifluoromethyl)phenylacetylene, respectively. This research was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas 'New Functionality Materials–Design, Preparation and Control' from the Ministry of Education, Science and Culture (no. 62 604 570).

REFERENCES

1 Masuda, T., Isobe, E., Higashimura, T. and Takada, K. *J. Am. Chem. Soc.* 1983, **105**, 7473
2 Takada, K., Matsuya, H., Masuda, T. and Higashimura, T. *J. Appl. Polym. Sci.* 1985, **30**, 1605
3 Shimomura, H., Nakanishi, K., Odani, H., Kurata, M., Masuda, T. and Higashimura, T. *Kobunshi Ronbunshu* 1986, **43**, 747
4 Ichiraku, Y., Stern, S. A. and Nakagawa, T. *J. Membrane Sci.* 1987, **34**, 5
5 Masuda, T. and Higashimura, T. *Adv. Polym. Sci.* 1986, **81**, 121
6 Petropoulos, J. H. *Adv. Polym. Sci.* 1985, **64**, 93
7 Paul, D. R. *Ber. Bunsenges. Phys. Chem.* 1979, **83**, 294
8 Stannett, V. T., Koros, W. T., Paul, D. R., Lonsdale, H. K. and Baker, R. W. *Adv. Polym. Sci.* 1979, **32**, 69
9 Isobe, E., Masuda, T., Higashimura, T. and Yamamoto, A. *J. Polym. Sci., Polym. Chem. Edn* 1986, **24**, 1839
10 Masuda, T., Isobe, E., Hamano, T. and Higashimura, T. *J. Polym. Sci., Polym. Chem. Edn* 1987, **25**, 1353
11 Niki, A., Masuda, T. and Higashimura, T. *J. Polym. Sci., Polym. Chem. Edn* 1987, **25**, 1553
12 Masuda, T., Yoshimura, T., Tamura, K. and Higashimura, T. *Macromolecules* 1987, **20**, 1734
13 Masuda, T., Tajima, H., Yoshimura, T. and Higashimura, T. *Macromolecules* 1987, **20**, 1467
14 Hamano, T., Masuda, T., Higashimura, T., Ueda, T. and Muramatsu, H. *Polymer Prepr. Jpn* 1986, **35**, 1352
15 Masuda, T., Hamano, T., Higashimura, T., Ueda, T. and Muramatsu, H. *Macromolecules* 1988, **21**, 281
16 Abe, Y., Masuda, T. and Higashimura, T. *J. Polym. Sci., Polym. Chem. Edn* submitted for publication
17 Gray, D. N. *Polym. Eng. Sci.* 1977, **17**, 719
18 Yasuda, H. and Stannett, V. 2nd Edn, Wiley–Interscience, New York, 1975, p. III-229
19 Stuart, H. A. 'Die Struktur des freien Molekuls', Springer-Verlag, Berlin, 1952, Ch. 12
20 van Amerongen, G. T. *Rubber Chem. Tech.* 1964, **37**, 1067
21 Robert, C. W., Melvin, J. A. and Williams, H. B. (Eds) 'CRC Handbook of Chemistry and Physics', 68th Edn, CRC Press, Florida, 1987, p. B-68
22 Itoh, Y. 'Zairyo to Suibun Handobukku' ('Handbook of Materials and Moisture') (Ed. H. Miyabe), Kyoritsu, Tokyo, 1968, p. 352
23 Stern, S. A., Shah, V. M. and Hardy, B. J. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1263
24 Nakagawa, T., Saito, T., Saito, Y. and Asakawa, S. *Polym. Prepr. Jpn* 1985, **34**, 1885
25 Lundstrom, J. E. and Bearman, R. J. *J. Polym. Sci., Polym. Phys. Edn* 1974, **12**, 97