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Local mobility of substituted polyacetylenes measured by quasielastic neutron scattering and its relationship with gas permeability

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Abstract

Local mobility of three substituted polyacetylenes was investigated by means of a quasielastic neutron scattering technique aiming at elucidating the origin of gas permeability of these polymers. It was found that the local flux, which is defined as the product of the relaxation rate Γ, and the mobile fraction f_m, increases with the gas permeability coefficient. This suggests that the local flux is an important factor controlling gas permeability. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Substituted polyacetylenes; Neutron scattering; Gas permeability

1. Introduction

In general, substituted polyacetylenes exhibit a relatively high gas permeability among all the examined polymers [1,2]. Among them, poly[1-(trimethylsilyl)-1-propyne] [poly (TMSP)] is a colorless solid polymer soluble in common solvents such as toluene and chloroform, and provides a free-standing membrane by solution casting. It shows an extremely high permeability to various gases: e.g. the oxygen permeability coefficient $P_{O_2} \sim 4000$ barrers [1 barrer $= 1(1 \times 10^{-10}$ cm^3 (STP)·cm/(cm^2·s·cmHg)] (25°C) [3–7]. This polymer shows unique features in the gas permeation behavior. For instance, it is glassy at room temperature unlike poly(dimethylsiloxane)[poly(DMS)], and its gas permeation is explained in terms of the dual-mode sorption and a diffusion mechanism, which involves both Langmuir-type sorption and Henry-type solution.

It was found several years ago that poly[1-phenyl-2-(*p*-trimethylsilylphenyl)acetylene] [poly(*p*-Me$_3$SiDPA)] also permeates gases fairly well [8,9]. Thus, its P_{O_2} value is 1100 barrers (25°C), corresponding to about 1/4 that of poly(TMSP) and about twice that of poly(DMS). Poly(*p*-Me$_3$SiDPA) is thermally much more stable than poly(TMSP), which will be an important factor when their practical application as separation membranes is considered. The high gas permeability of poly(TMSP) and poly(*p*-Me$_3$SiDPA) suggests that both stiff main chain and round-shaped side groups play an important role in the gas permeation through substituted polyacetylene membranes.

More recently, however, it has turned out that the P_{O_2} values (25°C) of poly[1-phenyl-2-(*p*-triisopropylsilylphenyl)-acetylene] [poly(*p*-*i*Pr$_3$SiDPA)] and poly[1-phenyl-2-(*p*-triphenylsilylphenyl)acetylene] [poly(*p*-Ph$_3$SiDPA)] are 20 and 3.8 barrers, respectively [10], which are much smaller than that of poly(*p*-Me$_3$SiDPA); this fact was rather unexpected to us. A possible explanation for the relatively low permeability of poly(*p*-*i*Pr$_3$SiDPA) and poly(*p*-Ph$_3$SiDPA) is that, if the round-shaped substituent is too large, its mobility is low, which leads to low permeability.

Inelastic and quasielastic neutron scatterings (INS and QENS) are powerful tools for the investigation of molecular motion. In the measurements, the scattering intensity is recorded as functions of energy and a momentum transfer of neutrons, providing information about both time and spatial scales of motion simultaneously. Generally speaking, quasielastic neutron scattering scans the ranges of 10^{-13}–10^{-8} s in time and of 1–600 Å in space, which are suitable for studying the motions of polymer molecules. Thus, many studies have so far been carried out on the dynamics of macromolecules [11,12]: e.g. reptation motions in polymer melts [13,14]; hydrodynamic interactions in polymer solutions [15]; dynamics in glassy states [16,17] and near glass transition temperature [18–20]; and rotational motions of methyl groups [21,22].

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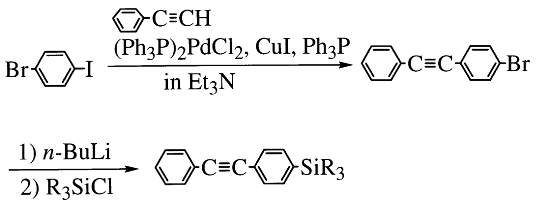

p-Me$_3$SiDPA (R = Me$_3$Si, overall yield 77%)
p-iPr$_3$SiDPA (R = iPr$_3$Si, overall yield 14%, mp 151.0–152.7°C)

Scheme 1.

In the present study, we investigate the local mobility of poly(TMSP), poly(p-Me$_3$SiDPA) and poly(p-iPr$_3$SiDPA) by means of a quasielastic neutron scattering technique to obtain information about whether the relatively low permeability of poly(p-iPr$_3$SiDPA) is caused by its low mobility.

2. Experimental

2.1. Monomer synthesis

1-Trimethylsilyl-1-propyne was purchased from Shin-etsu Chemical Industries Ltd., Japan and distilled twice from calcium hydride under nitrogen atmosphere. Diphenylacetylene derivatives were prepared by the method reported in the literature [9,10,23], according to Scheme 1. First, 1-(p-bromophenyl)-2-phenylacetylene was prepared through the Pd-catalyzed coupling reaction of p-bromoiodobenzene and phenylacetylene. Then, the bromine-containing derivative was lithiated with n-butyllithium, followed by the silylation of the resulting aryllithium with trimethyl- and triisopropylchlorosilanes to give two silyl-substituted diphenylacetylenes. Both monomers were purified by flash column chromatography and recrystallization. Anal. calcd for $C_{17}H_{18}Si$ (p-Me$_3$SiDPA): C 81.5, H 7.3, Si 11.2%. Found: C 81.7, H 7.2, Si 11.1, Anal. calcd for $C_{23}H_{30}Si$ (p-iPr$_3$SiDPA): C 82.6, H 9.1, Si 8.3%. Found: C 82.6, H 9.1, Si 8.3%.

2.2. Synthesis and characterization of polymers

Both $TaCl_5$ and Ph_3Bi were commercially obtained and used without further purification. Commercial n-Bu$_4$Sn was distilled twice from calcium hydride under the nitrogen atmosphere before use.

Table 1
Polymerization of TMSP, p-Me$_3$SiDPA and p-iPr$_3$SiDPA (polymerized in toluene at 80°C for 24 h)

Polymer	Yield (%)	M_N	M_W	M_W/M_N
Poly(TMSP)[a]	90	2.4×10^6	4.2×10^6	1.7
Poly(p-Me$_3$SiDPA)[b]	80	4.1×10^6	7.7×10^6	1.9
Poly(p-iPr$_3$SiDPA)[c]	82	5.4×10^6	9.5×10^6	1.7

[a] $[M]_0 = 1.0$ M; $[TaCl_5] = 10$ mM; and $[Ph_3Bi] = 10$ mM.
[b] $[M]_0 = 0.50$ M; $[TaCl_5] = 20$ mM; and $[n\text{-}Bu_4Sn] = 40$ mM.
[c] $[M]_0 = 0.10$ M; $[TaCl_5] = 20$ mM; and $[n\text{-}Bu_4Sn] = 40$ mM.

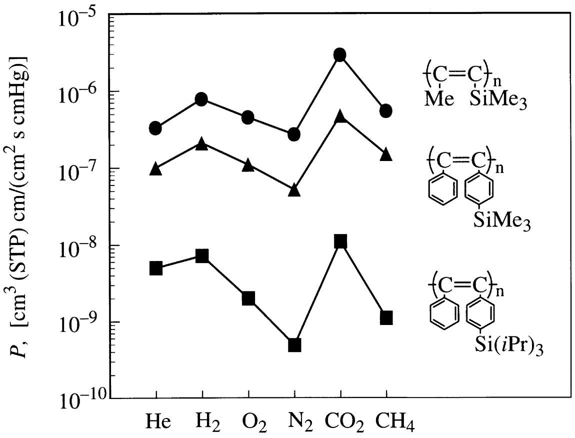

Fig. 1. Gas permeability coefficients (P) of polyacetylenes having silyl groups (25°C).

Polymerizations were carried out in toluene at 80°C for 24 h under dry nitrogen. The procedure for the polymerization of TMSP is described as an example [24,25]: a solution of $TaCl_5$ (72 mg, 0.20 mmol) and Ph_3Bi (88 mg, 0.20 mmol) in toluene (10 ml) was aged at 80°C for 15 min under dry nitrogen. Then, a solution of TMSP (2.25 g, 20.0 mmol) in toluene (10 ml) was added to the catalyst solution and the polymerization was carried out at 80°C for 24 h. The reaction mixture became viscous very quickly and eventually solidfied in a few minutes. The polymerization was quenched by adding a mixture (5 ml) of toluene and methanol (4:1 volume ratio). The polymer formed was dissolved in toluene (1 l), poured into a large amount of methanol (14 l), filtered off, washed with methanol, and finally dried under vacuum (yield 90%).

The molecular weights of polymers were determined by gel permeation chromatography (polystyrene calibration, eluent $CHCl_3$). The results of the polymerizations are summarized in Table 1.

2.3. Quasielastic neutron scattering measurements

Quasielastic neutron scattering measurements were performed with a cold triple-axis spectrometer HER at the beam port C1-1 of the JRR-3M reactor in Tokai, Japan. They were done with a fixed scattered wavenumber of $k_f = 1.25$ Å^{-1} and an energy resolution (FWHM) of about 0.2 meV using a horizontal focusing analyzer. Two types of scans were made at room temperature (296 K); i.e. an energy scan in a region of -0.2 to 3 meV at constant Q ($=1.9$ Å^{-1}) and an elastic Q-scan, Q being the magnitude of scattering vector. Motions observed under these experimental conditions are in a time range of $1.4 \times 10^{-12} - 2 \times 10^{-11}$ s and in a spatial scale at around 3.3 Å.

After correcting for background, the observed spectra were converted to differential scattering cross-sections

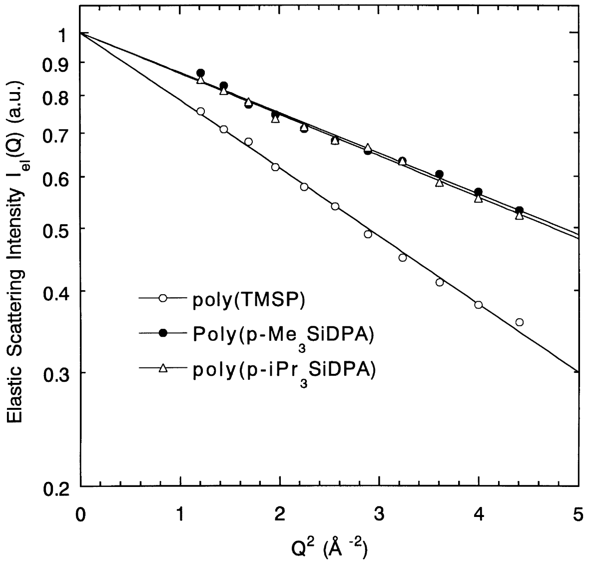

Fig. 2. Q dependence of elastic scattering intensity $I_{\mathrm{el}}(Q)$ for poly(TMSP), poly(p-Me$_3$SiDPA) and poly(p-iPr$_3$SiDPA).

$\partial^2\sigma/\partial\Omega\partial E$. In the samples used here, the observed differential scattering cross-section is dominated by incoherent scattering from hydrogen atoms because of its large incoherent atomic scattering cross-section [26]. Thus, we directly calculated the incoherent scattering laws $S(Q,\omega)$ from the data.

3. Results and discussion

3.1. Gas permeability of several substituted polyacetylenes

Fig. 1 represents the permeabilities of poly(TMSP), poly(p-Me$_3$SiDPA), and poly(p-iPr$_3$SiDPA) membranes to various gases as polygonal lines; these data are based on Refs. [6,9,10]. It is very clear that the gas permeability varies to a large extent, depending on the polymer structure, i.e. in the order of poly(TMSP) $>$ poly(p-Me$_3$SiDPA) $>$ poly(p-iPr$_3$SiDPA). It is a very interesting subject to elucidate the reason of such large variations. On the other hand, the patterns of these polygonal lines are very similar to one another, which suggests that the mechanisms of gas permeation through these polyacetylenes are essentially the same.

Table 2
Results of quasielastic neutron scattering for poly(TMSP), poly(p-Me$_3$SiDPA), and poly(p-iPr$_3$SiDPA)

Polymer	$\langle u^2\rangle$ (Å^2)	Γ (meV)	f_{m}
Poly(TMSP)	0.72	0.45	0.045
Poly(p-Me$_3$SiDPA)	0.44	0.34	0.012
Poly(p-iPr$_3$SiDPA)	0.43	0.21	0.0053

3.2. Elastic scattering

In order to obtain information on the atomic motion from the temperature factor, which gives the mean square displacement of H atoms, we first measured the elastic scattering. In Fig. 2, logarithm of the elastic scattering intensity $I_{\mathrm{el}}(Q)$ is plotted against Q^2 for poly(TMSP), poly(p-Me$_3$SiDPA) and poly(p-iPr$_3$SiDPA), where the elastic intensity is normalized to unity at $Q = 0$. In the Gaussian approximation [27], the Q dependence of incoherent elastic scattering intensity $I_{\mathrm{el}}(Q)$ is give by

$$I_{\mathrm{el}}(Q) = \exp[-\langle u^2\rangle Q^2/3] \tag{1}$$

for isotropic three-dimensional motions. Here, $\langle u^2\rangle$ is a mean square displacement of an atom. As seen in Fig. 2, the relation of Eq. (1) perfectly holds for the three samples, and hence we evaluated the mean square displacement $\langle u^2\rangle$ from the slopes of the straight lines. As mentioned above, the scattering intensities of the present samples are dominated by incoherent scattering from hydrogen atoms, so that $\langle u^2\rangle$ reflects the amplitudes of the motion of hydrogen atoms. The evaluated mean square displacements $\langle u^2\rangle$ are listed in Table 2. Poly(TMSP) has the largest $\langle u^2\rangle$ among them, which corresponds to the largest gas permeability coefficient as shown in Fig. 1. Probably the large amplitude of motions in poly(TMSP) accelerates the mobility of gases, leading to the large gas permeability.

3.3. Quasielastic scattering

For the purpose of obtaining information about the relaxational motions, we observed the quasielastic neutron scattering spectra or dynamic scattering laws $S(Q,\omega)$ of poly(TMSP), poly(p-Me$_3$SiDPA) and poly(p-iPr$_3$SiDPA) at 296 K, which are shown in Fig. 3. These spectra were normalized to the total scattering intensity in the present energy region of 0–3 meV. The dotted curve in the figure is the resolution function of the spectrometer. All the spectra contain the elastic scattering contribution within the resolution function, showing that there exist immobile molecules (or segments) and/or that such a motion is localized in a limited space [12]. In addition to the elastic scattering, the quasielastic spectral broadening is observed in an energy region below about 1.5 meV over the inelastic flat background indicated by dashed lines. The quasielastic and inelastic components originate from relaxational and vibrational motions in the polymers, respectively.

In order to analyze the spectra of Fig. 3, we assumed that the dynamic scattering law $S(Q,\omega)$ is phenomenologically described by

$$S(Q,\omega) = (1 - f_{\mathrm{m}})\delta(\omega) + f_{\mathrm{m}}S_{\mathrm{rel}}(Q,\omega) + B_{\mathrm{in}}(Q). \tag{2}$$

Here, $\delta(\omega)$ and f_{m} are a δ-function describing the scattering law from the immobile part and the fraction of the mobile part, respectively, and $S_{\mathrm{rel}}(Q,\omega)$ and $B_{\mathrm{in}}(Q)$ represent relaxational and vibrational spectra, respectively. Further, we

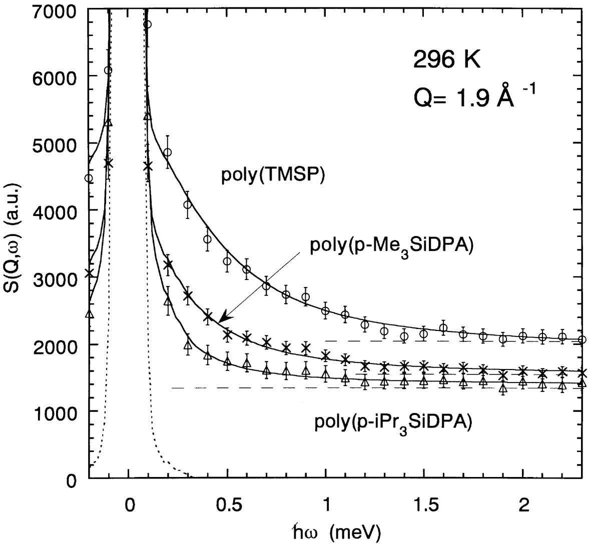

Fig. 3. Quasielastic neutron scattering spectra $S(Q,\omega)$ for poly(TMSP), poly(p-Me$_3$SiDPA) and poly(p-iPr$_3$SiDPA) measured at $Q = 1.9\ \text{Å}^{-1}$. The dotted curve is the resolution function of the spectrometer. The solid curves are the results of fits with Eq. (2) (see text). The dashed lines represent the inelastic contribution.

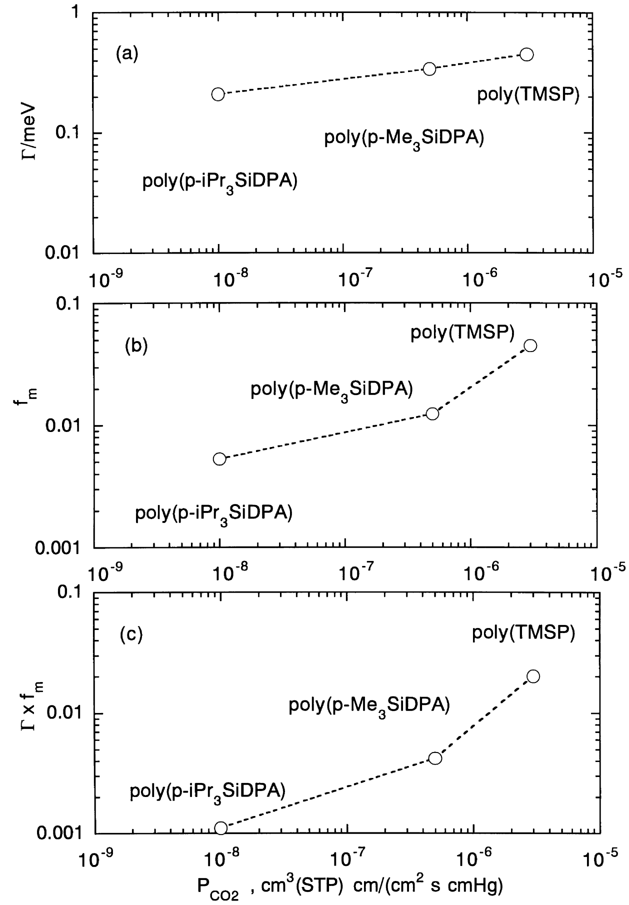

Fig. 4. (a) Relaxation rate Γ; (b) mobile fraction f_m; and (c) local flux $\Gamma \times f_m$ as a function of carbon dioxide permeability coefficient P_{CO_2}.

assumed that the relaxational spectrum $S_{rel}(Q,\omega)$ is described by a Lorentzian

$$S_{rel}(Q,\omega) = \frac{1}{\pi}\frac{\Gamma}{\Gamma^2 + \omega^2} \tag{3}$$

where Γ is the relaxation rate, corresponding to the inverse of the relaxation time $\tau(\Gamma = h/\tau$, h being Planck's constant). After convoluting the model function (Eq. (2)) with the energy resolution function of the spectrometer, we fitted it to the observed spectra. The solid curves in Fig. 3 show the results of the fits. The agreements are excellent, which confirms that the above simple phenomenological model can adequately describe the observed spectra.

We also analyzed the same spectra in terms of a three-site rotating jump motion [28] of methyl groups by taking into account their mobile fraction, because the incoherent scattering cross-section of methyl groups is much larger than the other scattering cross-sections. It was found that the relaxation (jump) rate of methyl protons and the mobile fraction evaluated in the three-site rotating model are almost the same as those in the above phenomenological model, which suggests that the quasielastic scattering intensity is mainly governed by the rotational motion of methyl groups in these polymers. In the case of poly(p-iPr$_3$SiDPA), strictly speaking, we have to take into account rotational motions of i-propyl group for a detailed analysis.

The evaluated relaxation rate Γ, and the mobile fraction f_m are summarized in Table 2. Both the relaxation rate and the mobile fraction decrease in the order of poly(TMSP) $>$ poly(p-Me$_3$SiDPA) $>$ poly(p-iPr$_3$SiDPA), and obviously depend on the molecular structure. Since the mobile fraction does not necessarily increase with increasing mobility in polymers, the observed correlation between the mobility and the mobile fraction is characteristic to these three polymers.

3.4. Relationship between the local mobility and the gas permeability

In order to see the relations of the relaxation rate and the mobile fraction to the gas permeability, Γ and f_m are plotted as a function of the CO$_2$ permeability coefficient P for the three polymers in Fig. 4(a) and (b), respectively. The larger the relaxation rate and the mobile fraction, the larger the permeability; this suggests that both the relaxation rate and the mobile fraction are important factors to determine the gas permeability. The local flux can be defined as the product of the relaxation rate and the mobile fraction, $\Gamma \times f_m$, and employed as a measure of local mobility. It is expected that the gas permeability is governed by the local flux. The local flux $\Gamma \times f_m$ versus the CO$_2$ permeability coefficient is plotted in Fig. 4(c). This plot strongly suggests the existence of a correlation between the local flux and the gas permeability. It is, however, noted that the local flux $\Gamma \times f_m$ of poly(p-iPr$_3$SiDPA) is about one order of magnitude smaller than that of poly(TMSP), while the gas permeability coefficient of poly(p-iPr$_3$SiDPA) is about two orders of magnitude lower than that of poly(TMSP) for several kinds of gases (see Fig. 1). A reason may be that the gas permeability coefficient (P) has been employed in place of the diffusion coefficient (D), which does not involve the factor of solubility (S) (however, the contribution of S to P is rather small and D is well correlated with P [6]).

The gas permeation through glassy polymers is explained in terms of the dual-mode mechanism, which postulates the presence of two phases, i.e. one governed by Langmuir sorption and the other controlled by Henry law [1,2]. Introduction of long n-alkyl and phenyl groups in substituted polyacetylenes generally decreases gas permeability [6], which is explicable by the decrease of molecular-scale voids and in turn by the decrease of the contribution of Langmuir term. On the other hand, the following explanation is plausible in the case of the polymers in the present study. We assume that Langmuir and Henry terms work in series, unlike the conventional idea that they work in parallel. It is rather unlikely that the presence of very bulky groups such as iPr$_3$Si and Ph$_3$Si, decreases the molecular-scale voids and hence Langmuir term will not vary largely among the present polymers. Then, the order of magnitude of gas permeability in the present polymers will be affected by Henry term, which is strongly governed by the local mobility. The present study has demonstrated a possibility that, besides the presence of molecular-scale voids, the local mobility of polymer molecules plays an important role in the gas permeability of glassy polymers.

In conclusion, we have revealed in the present study that there is a definite correlation between the gas permeability of poly(TMSP), poly(p-Me$_3$SiDPA) and poly(p-iPr$_3$SiDPA), and their local flux $\Gamma \times f_m$, and that this can explain the relatively low gas permeability of poly(p-iPr$_3$SiDPA).

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