

## Fast Dynamics of Substituted Polyacetylenes in Glassy States and its Relation to Gas Permeability

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We studied local dynamics of three substituted polyacetylenes in glassy states using a quasielastic neutron scattering technique in an energy range from -2 to 10 meV and found a clear correlation between the local mobility and the gas permeability in these polymers. On the basis of the  $Q$  dependence of the relaxation rate we will discuss possible motions related to the gas permeability.

KEYWORDS: quasielastic neutron scattering, local mobility, gas permeability, substituted polyacetylenes

### §1. Introduction

It is well known that some substituted polyacetylenes show high gas permeability among all the examined polymers.<sup>1,2)</sup> In particular, poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] exhibits extremely high permeability to various gases; e. g., the oxygen permeability coefficient  $P_{O_2}$  4000 barrers [1 barrer =  $1(1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ s cmHg}]$  (25 °C)], which is usually explained by the dual mode sorption (Langmuir-type and Henry-type sorptions) and diffusion.

Masuda *et al.*<sup>3-5)</sup> synthesized a variety of substituted polyacetylenes and investigated the relationship between gas permeability and side-group structure. Through these studies, they obtained some indications that the local mobility of substituted polyacetylenes in glassy states plays an important role in their gas permeability. Stimulated by this finding, we investigated the local mobility of three substituted polyacetylenes: poly(TMSP), poly[1-phenyl-2-(*p*-trimethyl silylphenyl) acetylene] [poly(*p*-Me<sub>3</sub>SiDPA)] and poly[1-phenyl-2-(*p*-triisopropyl silylphenyl) acetylene] [poly(*p*-iPr<sub>3</sub>SiDPS)] by means of quasielastic neutron scattering (QENS) to find a positive relation between the gas permeability and the local mobility.<sup>6)</sup> In these measurements, two types of scans were performed using high resolution triple axis spectrometer (HER/TAS) with an energy resolution of 0.2 meV: an energy  $\hbar\omega$  scan from -0.2 to 3 meV at a constant  $Q = 1.9 \text{ \AA}^{-1}$  ( $Q$  being length of scattering vector) and a  $Q$  scan from 0.2 to 2.4  $\text{\AA}^{-1}$  at an elastic position ( $\hbar\omega = 0$ ). Although a clear relation between gas permeability and local mobility was observed, it was difficult to discuss what kinds of motions are related to the gas permeability due to the limited  $\hbar\omega$  and  $Q$  ranges. In the present measurements, we therefore extended the energy  $\hbar\omega$  range to 15 meV and the  $Q$  range to 2.6  $\text{\AA}^{-1}$  using a time-of-flight (TOF) spectrometer with an energy resolution of 0.08 meV. On the basis of the wide  $\hbar\omega$  and  $Q$  data we will discuss possible motions related to the gas

permeability.

### §2. Experimental

Poly(TMSP), [poly(*p*-Me<sub>3</sub>SiDPA)] and [poly(*p*-iPr<sub>3</sub>SiDPS)] were obtained by polymerizing the corresponding monomers. The procedure of the polymerization was described in detail in the preceding paper.<sup>6)</sup> The weight-average molecular weights  $M_w$  of poly(TMSP), [poly(*p*-Me<sub>3</sub>SiDPA)] and [poly(*p*-iPr<sub>3</sub>SiDPS)] are  $4.2 \times 10^4$ ,  $7.7 \times 10^6$  and  $9.5 \times 10^6$  and the polydispersities in terms of  $M_w/M_n$  ( $M_n$  being number average molecular weight) are 1.7, 1.9 and 1.7, respectively. The glass transition temperatures are much higher than room temperature although the exact values are not measurable due to the chemical decompositions.

Quasielastic neutron scattering measurements were performed on a TOF spectrometer AGNES installed at C3-1 cold neutron guide in JRR-3M reactor, Tokai. The energy resolution is 0.08 meV at the elastic position and the  $Q$  range is 0.2 to 2.6  $\text{\AA}^{-1}$ . After subtracting empty can scattering, the observed TOF spectra were converted to dynamics scattering laws  $S(Q, \omega)$ . For the analysis, model functions were fitted to  $S(Q, \omega)$  after convoluting with the resolution function evaluated by a vanadium measurement.

### §3. Results and Discussion

Fig. 1 shows a dynamic scattering law  $S(Q, \omega)$  of poly(TMSP) in an energy region from -2 to 10 meV. The spectrum was obtained by summing up 10 spectra to get higher counting statistics and the average  $Q$  value is 1.5  $\text{\AA}^{-1}$ . The measurement was done at 296 K which is enough below the glass transition temperature  $T_g$ , but the spectrum shows quasielastic broadening, suggesting that some parts of poly(TMSP) are moving stochastically. Modes of this motion will be discussed later.

In the preceding paper,<sup>6)</sup> we have analyzed the dynamic scattering law  $S(Q, \omega)$  in the energy range from -0.2 to 2.5 meV assuming that the quasielastic com-

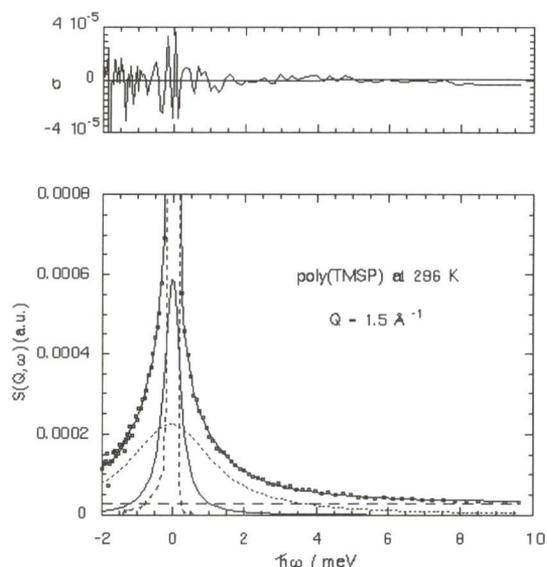


Fig. 1. Dynamic scattering law  $S(Q, \omega)$  of poly(TMSP) at 296 K. The spectrum was obtained by summing up ten spectra and the average value of  $Q$  is  $1.5 \text{ \AA}^{-1}$ . The curves are results of fit with the model function consisting of elastic (dashed), narrow quasielastic (solid), broad quasielastic (dotted), and inelastic (long dashed) components.

ponent is described by a single Lorentzian. However, this cannot be in the range from -2 to 10 meV. Then, we employed two Lorentzian functions to describe the quasielastic component, and hence the model function is now given by

$$S(Q, \omega) = (1 - A_n(Q) - A_b(Q))\delta(\omega) + A_n(Q)L(\Gamma_n, \omega) + A_b(Q)L(\Gamma_b, \omega) + B_{in}(Q). \quad (3.1)$$

where  $A_n(Q)$  and  $A_b(Q)$  are the fractions of the narrow and broad quasielastic component,  $L(\Gamma_i, \omega)$  is a Lorentzian function with half-width at half-maximum (HWHM)  $\Gamma_i$  ( $i = n, b$ ) and  $B_{in}(Q)$  is an inelastic flat background. This model function was fitted to the observed  $S(Q, \omega)$  and the results of fit are given in Fig. 1, showing a very good agreement. We then evaluated the relaxation rates (HWHM)  $\Gamma_n$  and  $\Gamma_b$  of the narrow and broad quasielastic components from the fits, and plotted them against the permeability coefficient of  $O_2$  ( $P_{O_2}$ ) in Fig. 2.

The values of  $\Gamma_b$  are independent of  $P_{O_2}$  while  $\Gamma_n$  shows a correlation with  $P_{O_2}$ , suggesting that the narrow quasielastic component is related to the gas permeability. In order to see the relation between the local mobility and gas permeability, we employ local flux  $F$  as a measure of the local mobility following the previous treatment,<sup>6)</sup> which is defined as a product of the relaxation rate  $\Gamma_n$  and the fraction  $A_n$  of the narrow component. The local flux  $F$  is plotted versus the permeability coefficient  $P_{O_2}$  in Fig. 3, showing a good correlation. In the figure, we also plotted  $F$  previously evaluated in a single Lorentzian fit in the energy region from -0.2 to 2.5 me. Both the local fluxes show similar correlations with

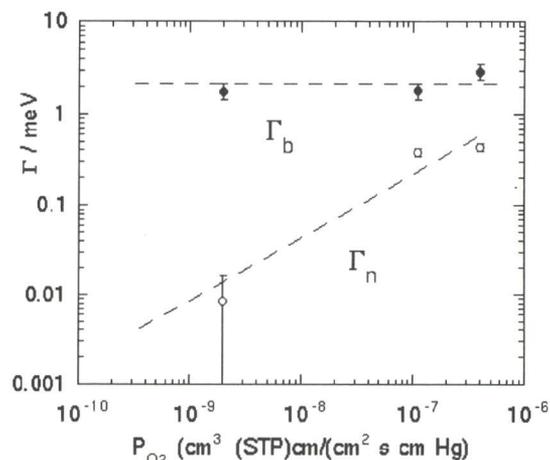


Fig. 2. Relaxation rates (HWHM) of the narrow and broad quasielastic components,  $\Gamma_n$  and  $\Gamma_b$ , versus gas permeability coefficient of  $O_2$  ( $P_{O_2}$ ).

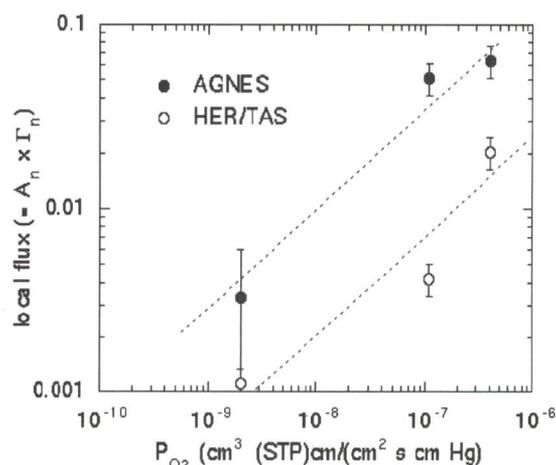


Fig. 3. Local flux  $F (= \Gamma_n \times A_n)$  as a function of gas permeability coefficient of  $O_2$  ( $P_{O_2}$ ). (●): from the double Lorentzian fit (this work), (○): from the single Lorentzian fit<sup>6)</sup> (see text).

the gas permeability though the present value is larger than the previous one. This is not surprising because the inelastic flat background in the single Lorentzian fit is mostly included in the broad component in the double Lorentzian fit. In any case, the correlation between  $F$  and  $P_{O_2}$  strongly suggests that the gas permeability of substituted polyacetylenes are related to the local mobility. In the following we discuss about what kinds of motions the broad and narrow quasielastic components are on the basis of the  $Q$  dependence of the relaxation rates.

The  $Q$  dependences of the relaxation rates are shown in Fig. 4 for poly(TMSP) as an example. The relaxation rate of the broad component  $\Gamma_b$  is almost independent of  $Q$  while that of the narrow component increases with  $Q$ . Relaxation rates of other two polymers also show similar

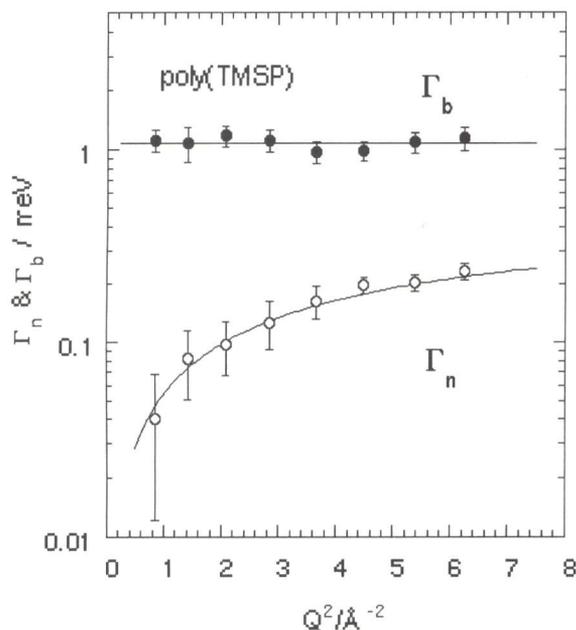


Fig. 4.  $Q$  dependence of relaxation rates (HWHM) of the narrow and broad quasielastic components,  $\Gamma_n$  and  $\Gamma_b$ . Solid curve for  $\Gamma_n$  is a result of the jump diffusion model fit, giving a root mean squared jump distance  $\langle l^2 \rangle^{0.5}$  of 0.83 Å.

behavior. The fact that  $\Gamma_b$  is independent of  $Q$  can be interpreted that the broad quasielastic component is a localized mode.

In the last two decades, dynamics of glassy polymers was extensively studied by means of QENS.<sup>7)</sup> These studies have revealed that a broad excitation peak, the so-called Boson peak, is universally observed in glasses far below  $T_g$ . As temperature increases, a picosecond fast process appears in an energy below about 3 meV. Onset temperature of the fast process is at round  $T_g$  for polymers having no large side chains,<sup>8-10)</sup> while it is far below  $T_g$  for polymers with long side chains and/or many internal degrees of freedom.<sup>11,12)</sup> What we have to emphasize here is that  $S(Q, \omega)$  of the fast process is well described by a Lorentzian and the relaxation rate is independent of  $Q$ . These features of the fast process are very similar to those observed for the broad quasielastic component in poly(TMSP), implying that it is attributable to the fast process commonly observed in glassy polymers. On the other hand, the relaxation rate of the narrow quasielastic component increases with  $Q$ . This  $Q$  dependence means that the motion is not a torsional motion of methyl groups but somewhat diffusive. Of course, this diffusive motion is not spreaded in an infinite space because it is in the glassy state. Such diffusive motion has never been observed in polymers having no large side chains below  $T_g$  as far as we know. Hence, it is considered that it is caused by the large side chains in poly(TMSP). Note that the Boson peak contribution is not directly taken into account in the present data analysis, which is implicitly included in the inelastic flat background, be-

cause the Boson peak is very weak in intensity compared to the quasielastic contributions.

As a first step, we try to describe this diffusive motion in terms of the jump diffusion model. In this model, it is assumed that an atom (or an atomic group) stays in a quasi-equilibrium sites for a rest time  $\tau_0$ , and often jumps out to another site with an average jump time  $\tau_1$  and a root mean squared jump distance of  $\langle l^2 \rangle^{0.5}$ . This model was generally formulated by Singwi and Sjolander.<sup>13)</sup> Neglecting local vibrations in the quasi-equilibrium site, the dynamic scattering law  $S(Q, \omega)$  in the case<sup>14)</sup> of  $\tau_0 \gg \tau_1$  is given by

$$S(Q, \omega) = \frac{1}{\pi} \frac{\Gamma_j}{\omega^2 + \Gamma_j^2} \quad (3.2)$$

$$\Gamma_j = \frac{DQ^2}{1 + DQ^2\tau_0} \quad (3.3)$$

where  $D$  is an apparent diffusion coefficient given by  $\langle l^2 \rangle / 6\tau_0$ . The theoretical  $S(Q, \omega)$  is given by a Lorentzian, agreeing with the observed functional form of  $S(Q, \omega)$ . Hence, we fitted the theoretical  $Q$  dependence of relaxation rate  $\Gamma_j$  (HWHM) to the observed one as shown by a solid curve in Fig. 4. The fitted curve well describes the observed  $Q$  dependence, implying that the jump diffusion model is not bad to describe the motion. From this fit we found that the root mean squared jump distance  $\langle l^2 \rangle^{0.5}$  and the rest time  $\tau_0$  are 0.83 Å and 2.1 ps, respectively. Judging from these values, the motion related to the gas permeability is very much localized in space and time.

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