Dynamics of Polysilane Chain in Dilute Solution as Studied by Spin Labeling[1]

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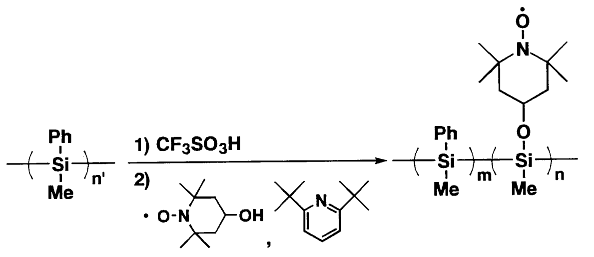
The rotational relaxation times and the rotational energy barriers of spin-labeled poly(phenylmethyl)silane were estimated in four different dilute solvents by the line shape analysis of the ESR signals.

We wish to report herein the first detailed study of the local segmental dynamics of spin-labeled poly(phenylmethylsilane) in dilute solutions by the line shape analysis of their electron spin resonance (ESR) signals.

An ESR relaxation measurement of spin-labeled polymers in dilute solution is able to characterize local segmental rotational motions. A line-width analysis of the ESR spectra of stable nitroxide radicals in a polymer chain gave useful information on the dynamics of the chain.[2] Analysis of the local segmental motion of polysilanes is of special interest in relation to the peculiar physical properties of polysilanes,[3] although no spin-labeled polysilane is reported to date.

A spin-labeled poly(phenylmethylsilane) ($\bar{M}$n = 2.4×10^{4}) was prepared in 83 % yield by partial removal of phenyl groups from poly(phenylmethylsilane) with trifluoromethane sulfonic acid[4] followed by treatment with 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy (4-hydroxy-TEMPO, free radical) as shown below.



Analysis of the spin-labeled polymer by gel permeation chromatography (GPC, polystyrene standard) demonstrated that no degradation occurred in the spin-labeling process. To avoid the possible line broadening by spin exchange, the spin density was kept as below as one nitroxide radical per a few monomer units. For example, the polysilane with one nitroxide radical per 13 phenylmethylsilyene unit was used. The content of the nitroxide in the polymer was determined by ^{1}H NMR spectra. A solution of spin-labeled poly(phenylmethylsilane) in toluene (2.5% by weight) was prepared and was subjected to the measurement of the variable temperature ESR spectra from −50 to +50 °C. A typical example of the ESR spectra of the spin-labeled poly(phenylmethylsilane) in toluene solution at room temperature is shown in Figure 1.

Freed[5] and Kivelson[6] have investigated the relationship between the ESR line shapes and the correlation times of the rotational motion (τ). The kinetics of the conformational changes of polymer backbones has been investigated by Kramers, whose theory[7] provides a commonly used framework for quantitative interpretation of molecular dynamics in solution. Helfand has thus applied the Kramers' theory for conformational transitions of polymers.[8] The correlation times of the rotational motion (τ) were predicted to obey an Arrhenius-type equation:

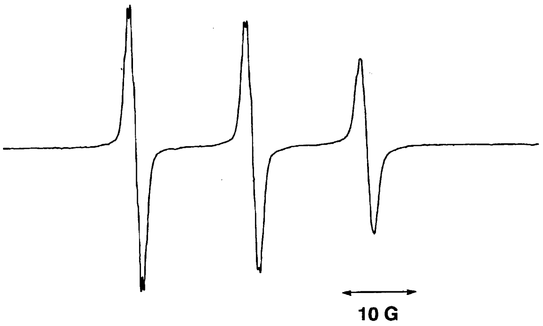


Figure 1. ESR spectra of spin-labeled poly(phenylmethylsilane) in dilute toluene solution at room temperature.

$$1/k = \tau = A\exp(Ea/RT) \tag{1}$$

where A is a constant independent on temperature, R is the gas constant, T is the absolute temperature, and Ea is a rotational barrier for the single-bond rotation in the polymer chain. The ESR line shape analysis gave the rotational correlation rate constants (k) of spin-labeled poly(phenylmethylsilane) which were found to obey the Arrhenius-type equation. Fig. 2 shows the Arrhenius plots in four different solvents. The rotational energy barrier for the local segmental dynamics of the polysilane in dilute solution can be derived from these measurements; for example, the value in dilute toluene is 15.9 kJmol^{-1}.

It is noteworthy that the observed rotational energy barrier (Ea) obtained from the plots of logk vs 1/T should be the sum of the true rotational energy barrier (Ea*) and solvent activation energy (Eη):

$$Ea = Ea^{*} + \alpha E\eta \tag{2}$$

where α is an auto correlation function.[9]

Then next, viscosity dependence of the local segmental dynamics was examined in order to estimate the true rotational energy barrier (Ea*) of poly(phenylmethylsilane). As shown in Fig. 2, all the rotational correlation rate constants, derived from the ESR spectra of spin-labeled poly(phenylmethylsilane) in four solvents,[10] *i.e.*, toluene, cyclohexane, *cis*-decalin, and squalane, were found to fit the Arrhenius-type equation. The

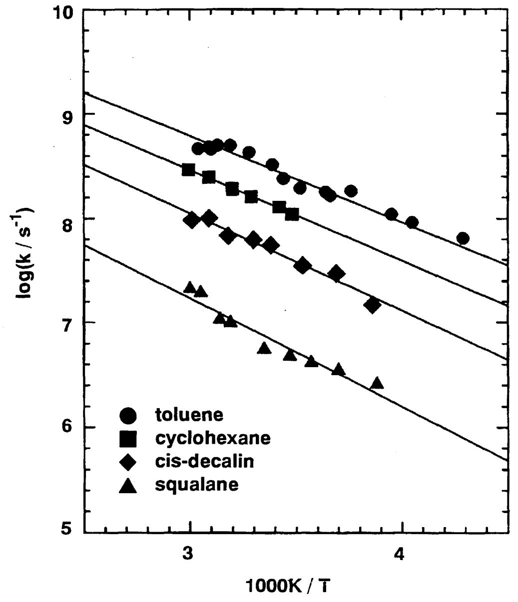


Figure 2. Arrhenius plots of the correlation rate constants for spin-labeled poly(phenylmethylsilane): (●) in toluene; (■) in cyclohexane; (◆) in cis-dcalin; and (▲) in squalane.

Table 1. ESR Relaxation Parameters for Spin-Labeled Poly-(phenylmethylsilane) in Various Solvent[a]

solvent	Ea/kJmol^{-1}	A/s^{-1}
toluene (8.8)	15.9	2.0x10^{11}
cyclohexane(12.0)	16.7	1.3x10^{11}
cis-decalin (14.2)	18.0	7.9x10^{10}
squalane (32.9)	25.3	1.6x10^{11}

[a] Values in parentheses are viscosity of the solvents (Eη).

rotational activation energies were calculated and listed in Table 1.

An auto correlation function (α) was then calculated to be 0.4 from the best fit slope of a plot of Ea vs Eη (Fig. 3). Thus, the best estimate of the true rotational energy barrier (Ea*) for local dynamics in poly(phenylmethylsilane) from these measurements is 12.2 kJmol^{-1}.

The present method can be applied to the study on the substituent effect of polysilanes on the rotational energy barriers, which should be interesting in relation to the thermochromism of polysilanes. The results will be reported in a forthcoming paper.

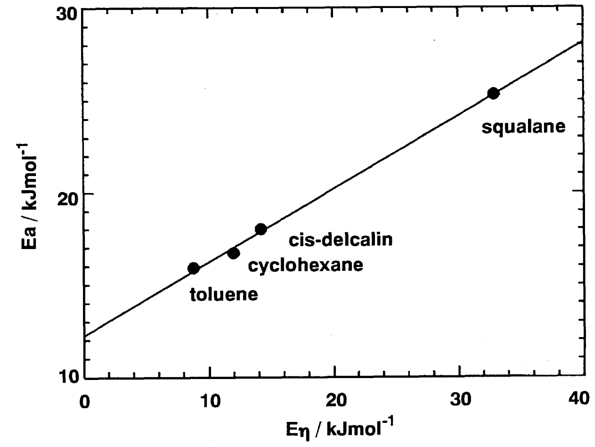


Figure 3. Viscosity dependence of the rotational activation energies in four solvents.

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References and Notes

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