Hydrodynamic Behavior and Semiflexibility of a Disubstituted Polyacetylene with Silyl Group, Poly[(1-trimethylsilyl)-1-propyne], in Dilute Solution

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Dynamic light scattering, viscosity, sedimentation velocity measurements were made on poly[(1-trimethylsilyl)-1-propyne] fractions in benzene and THF. The hydrodynamic behavior derived from the diffusion and sedimentation coefficients, the internal mode motions, and the intrinsic viscosity in benzene at 30℃ indicated that the present polymer is a semiflexible chain with the following molecular parameters expressed in terms of the wormlike cylinder model ; the persistence length $\lambda^{-1}/2$=32.5nm, the molecular mass per unit contour length M_L=400nm^{-1}, and the cylinder diameter d=1.1nm.

Keywords: Polyacetylene derivatives/ Semiflexible chain/ Dynamic light scattering/ Translational diffusion coefficient/ Sedimentation coefficient/ Intrinsic viscosity

Although polyacetylene is virtually insoluble in any solvent, the disubstituted polyacetylenes in which two hydrogens are replaced by alkyl and phenyl groups are soluble in ordinary organic solvents and show solution behavior characteristic of the semiflexible polymers. Poly[(1-trimethylsilyl)-1-propyne] (PMSP) is a disubstituted polyacetylene which contains the silyl group instead of phenyl one; -$[C(CH_3)=C(Si(CH_3)_3)]_n$-. This polymer is in the glassy state at room temperature but has extremely high permeability for various gases in the solid film[1]. These features are distinguished clearly from those of usual disubstituted polyacetylenes, suggesting steric effects and high molecular mobility due to the silyl group. Since PMSP dissolves in benzene and THF (good solvents), it is interesting to compare the solution behavior with that of an usual disubstituted polyacetylene, poly(1-phenyl-1-propyne) (-$[C(CH_3)=C(C_6H_5)]_n$-, PPP), which shows the semiflexibility even in a good solvent, toluene[2].

The PMSP sample, a gift from Prof. T. Masuda, Kyoto University, was separated into 14 fractions by repeated precipitation fractionations in benzene-methanol mixtures and freeze-dried from filtered benzene solutions. Their hydrodynamic characteristics were determined through dynamic light scattering, sedimentation, and viscosity experiments in benzene at 30℃ : the translational diffusion coefficient D, the sedimentation coefficient s, their first concentration-dependence coefficients (the hydrodynamic virial

FUNDAMENTAL MATERIAL PROPERTIES —Molecular Motion Analysis—

scope of research

The research activities in this subdivision cover structural studies and molecular motion analyses of polymers and related low molecular weight compounds in the crystalline, glassy, liquid crystalline, and solution states by high-resolution solid-state NMR, dynamic light scattering, electron microscopy, and so on, in order to obtain basic theories for the development of high-performance polymer materials. The processes of biosynthesis, crystallization, and higher-ordered structure formation are also studied for bacterial cellulose.

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coefficients) k_D and k_S, the intrinsic viscosity [η], and the decay rates for the dynamical modes of motions Γ_i(i=1,2) were analyzed.

When D and s are expanded in a series of the polymer mass concentration c about the infinite dilution values D_0 and s_0, i.e., $D=D_0(1+k_Dc)$ and $s^{-1}=s_0^{-1}(1+k_Sc)$, the coefficients k_D and k_S represent the hydrodynamic and/or thermodynamic interactions of the polymers and are related by the relation $k_D+k_S=2A_2M_W$ to the second virial coefficient A_2, a measure of the thermodynamic intermolecular interactions. Here M_W denotes the weight-average molecular weight of the polymer. As typically shown by k_D=-311 and k_S=314 cm^3g^{-1} for fraction 4 of PMSP($M_W=6.98\times10^5$), A_2 of PMSP was found to be zero to within experimental errors, indicating little intermolecular excluded volume effects. This means that PMSP is in the unperturbed state in benzene at 30℃. However, [η] did not show the linear relation between [η] and $M_W^{1/2}$, as should be for the unperturbed chains. Rather, the plot of $(M_W^2/[\eta])^{1/3}$ against $M_W^{1/2}$ (Bohdanecky plot, Fig.1) was found to be linear in all the region of M_W measured, the intercept being not equal to zero but positive difinite. PMSP in benzene at 30℃ is thus a semiflexible polymer and the intramolecular excluded volume interactions were not appreciable at M_W up to 7×10^5.

The semiflexible chain parameters of PMSP were estimated by analyzing the viscosity data in terms of a wormlike cylinder model of the diameter d, the persistence length $\lambda^{-1}/2$, the contour length L, and the molecular mass per unit contour length $M_L=M_W/L$. The Bohdanecky expression for [η], $(M_W^2/[\eta])^{1/3} = A+BM_W^{1/2}$, gives the parameters M_L and λ^{-1}/M_L with $A=A_0M_L\Phi_\infty^{-1/3}$, $B=B_0(\lambda^{-1}/M_L)^{-1/2}$ and A_0 and B_0 the function of d/λ^{-1}. Adopting the diameter d=1.1± 0.2nm from the crystallographic data of polyacetylene and $\Phi_\infty=2.17\times10^{23}mol^{-1}$, we obtained the chain parameters of PMSP to be $\lambda^{-1}/2$=3.25nm and M_L=400 nm^{-1}. In Table 1 these values are compared with those of PPP and typical cellulose derivatives, i.e., cellulose acetate (CA) and hydroxypropyl cellulose (HPC)[3]. The axial ratio of Kuhn segment $X_k=\lambda^{-1}/d$ =5.9 for PMSP in benzene is smaller than that of PPP in toluene, 6.9, indicating that PMSP behaves as a wormlike chain but its rigidity is lower than that of the phenyl-substituted polyacetylene, PPP, as well as the usual cellulose derivatives in dimethylacetamide(DMAc). In Figure 2 is shown the scattering vector (q) dependence of the first cumulant Γ_e for PMSP in benzene at 30℃. Γ_e, the decay rate of the scattered-intensity time-correlation function at time $\to 0$, gives us information on whole modes of motions in the wormlike chain, i.e., the translational diffusion, the rotational diffusion, the anisotropy of the translational diffusion, the internal modes of motions and so on. Γ_e/D_0q^2 increases gradually with increasing qL. However, it never approaches to a plateau, the characteristic feature of rigid rods, and deviates upward drastically. This deviation seems to exceed the behavior of typical wormlike chains of high stiffness(a chain line) and indicates that the intrachain flexibility becomes effective. These double-stepped increase of Γ_e/D_0q^2 with increasing qL certifies that PMSP in benzene is a relatively flexible wormlike chain.

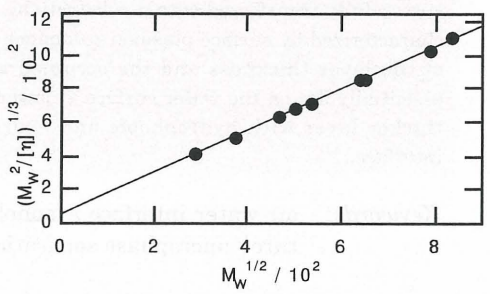

Figure 1. Bohdanecky plot for PMSP in benzene at 30℃.

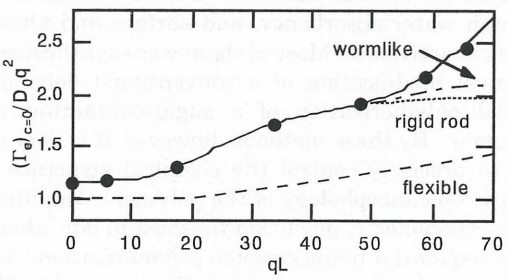

Figure 2. Plot of $(\Gamma_e)_{c\to0}/D_0q^2$ vs. qL for PMSP in benzene at 30℃.

Table 1. Axial ratio for wormlike chain polymers

polymer	solvent	X_k	$\lambda^{-1}/2$(mm)	d(mm)
PMSP	benzene	5.9	3.3	1.1
PPP	toluene	6.9	3.9	1.1
CA(2.5)	DMAc	17.3	7	0.81
HPC	DMAc	13.5	7	1.04

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