Solution Properties of 1,3-Cyclohexadiene Polymers by Laser Light Scattering and Small-Angle Neutron Scattering

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Introduction

1,3-Cyclohexdiene polymers (PCHD) and their derivatives are of interest due to the six-member rings in the main chain, which are expected to impart higher mechanical strength and better thermal and chemical stability, as compared to common vinyl polymers.[1] For example, hydrogenated PCHD has the highest glass transition temperature ($T_g \sim 231$ °C) of all hydrocarbon polymers, and it also shows good heat, weather, impact, abrasion, and chemical resistance as well as low water absorption.[1] In addition, PCHD has unique photochemical properties, such as excellent transparency, due to the isolated double bonds in the main chain.[2,3] Also, block copolymers containing PCHD show unusual phase separation behavior. For example, a styrene/1,3-CHD block copolymer (PS-*b*-PCHD) with 50 vol % CHD (1,4/1,2 ∼ 95/5) exhibits a core−shell or hollow cylinder morphology, while a typical styrene/acyclic diene (isoprene or butadiene) block copolymer with similar composition exhibits a lamellar structure.[4] Such phase behavior and many other properties strongly depend on the conformation of the polymer in solution or bulk.[5] However, almost no data have been reported on the conformation of PCHD, probably because of the lack of well-defined and well-characterized samples. Here we report solution properties of PCHD in tetrahydrofuran (THF) and chloroform by multiangle laser light scattering, viscometry, and small-angle neutron scattering (SANS).

Experimental Section

Well-defined PCHD samples with different molecular weights and similar microstructures (1,4/1,2 ∼ 94/6) were prepared according to literature procedures.[6] Light scattering was performed in THF on a Wyatt DAWN EOS instrument over an angular range from 38° to 147° using laser light at 690 nm. The specific refractive index increments (d*n*/d*c*) of PCHD in THF at 40 and 50 °C were determined to be 0.171 and 0.174 mL/g, respectively, using an OPTILAB DSP refractometer (690 nm). Intrinsic viscosities ([η]) of PCHDs were measured in THF at 40 and 50 °C and also in chloroform at 40 °C using a Polymer Laboratories PL-120 size exclusion chromatography (SEC) system equipped with a capillary differential viscometer (Viscotek) and a refractive index (RI) detector. Radii of gyration (R_g) were measured by using the PL-120 SEC-equipped with a two-angle (15° and 90°) light scattering photometer (PD2020) and a RI detector in THF at 40 °C. Two PL-gel 10 mm MIXED-B columns were used with a flow rate of 1 mL min^{-1}. A polystyrene standard (50K) was used to calibrate the 90° detector.

Small-angle neutron scattering (SANS) measurements were carried out on the NG3 30 m instrument[7] at the National Institute of Standards and Technology (NIST) Gaithersburg, MD, and also on the SANS-1 facility[8] at the Paul Scherrer Institute (PSI), Villigen, Switzerland. The neutron wavelength (λ) was 0.6 nm at both facilities, and the sample−detector distances were 2 m (NIST) and 4.5 m (PSI). The data were corrected for instrumental backgrounds and the (minimal) parasitic scattering from the quartz cells that contained the solutions. Corrections were also applied for the variation of the detector efficiency on a cell-by-cell basis, prior to radial averaging to give an overall range of momentum transfer $0.19 < Q < 3.00$ nm^{-1} (NIST) and $0.15 < Q < 1.80$ nm^{-1} (PSI), where $Q = 4\pi\lambda^{-1} \sin\theta$ and 2θ is the angle of scatter. The net intensities were converted to an absolute differential cross section per unit sample volume [dΣ(Q)/dΩ in units of cm^{-1}], as previously described.[9,10] Procedures for calculating the incoherent background, arising largely from the protons in the sample, have been described previously.[11] The SANS cross section was measured as a function of polymer concentration, temperature, and solvent quality.

Results and Discussion

Intrinsic Viscosities. The molecular weight dependence of [η] for PCHD in THF and chloroform is shown in Figure 1. The straight lines fitting our data for PCHD are expressed by

$$[\eta] = 0.12 M_w^{0.52} \quad (\text{cm}^3\ \text{g}^{-1} \text{ in THF at } 40\ ^\circ\text{C}) \qquad (1)$$

$$[\eta] = 0.059 M_w^{0.63} \quad (\text{cm}^3\ \text{g}^{-1} \text{ in chloroform at } 40\ ^\circ\text{C}) \qquad (2)$$

The small exponents of 0.52 and 0.63 indicate that this polymer has a flexible conformation in solution. The [η] of a wormlike chain is calculated for the touched-bead wormlike chain model by[12]

$$[\eta] = f(\lambda L, \lambda d)/(\lambda^3 M) \qquad (3)$$

where L, λ^{-1}, and d_B are the contour length, the Kuhn segment length, and the diameter of a bead, respectively. The first parameter is related to the molecular weight M by $L = M/M_L$, with M_L being the molar mass per unit contour length of the polymer chain. The contour length L per monomer unit for the polymer consisting of the1,4-isomer was estimated to be 0.41 ± 0.03 nm, and M_L can be calculated to be 200 ± 15 nm. We note that in principle the three parameters should be determined by fitting [η] as a function of M; however, the fitting is not possible because of the low exponent of [η] vs M_w. From curve-fitting procedures, λ^{-1} and d_B values were determined to be $\lambda^{-1} = 1.8_5 \pm 0.1_5$ nm and $d_B = 0.5_3 \pm 0.0_7$ nm in chloroform and $\lambda^{-1} = 1.3_0 \pm 0.1$ nm and $d_B = 0.5_7 \pm 0.0_6$ nm in THF. The Kuhn segment length thus obtained is close to that of typical flexible polymers (e.g., polystyrene, $\lambda^{-1} = 2$ nm).[13] On the other hand, the d_B value of about 0.6 nm is smaller than that of polystyrene ($d_B \sim 1.0$ nm)[14] or poly(*n*-hexyl isocyanate) ($d_B \sim 1.6$ nm),[15] with bulky side groups, but identical to the 0.6 nm value for polyisobutylene[16] with small side groups. R_g for PCHD-1

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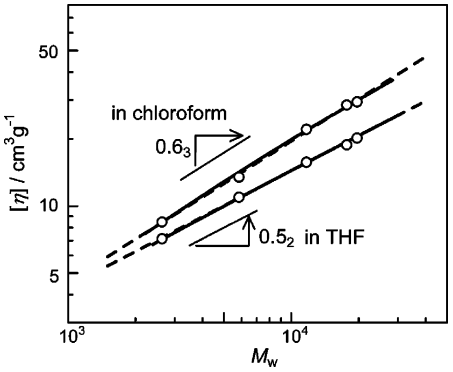

Figure 1. Molecular weight dependence of $[\eta]$ for PCHD in indicated solvents at 40 °C (THF) and 50 °C ($CHCl_3$). Dashed lines: calculated by eq 1. Solid curves: theoretical values for the touched-bead wormlike chain model with $M_L = 200$ nm^{-1}, $\lambda^{-1} = 1.8_5$ nm, $d_B = 0.5_3$ nm (in chloroform) and $M_L = 200$ nm^{-1}, $\lambda^{-1} = 1.3_0$ nm, $d_B = 0.5_7$ nm (THF).

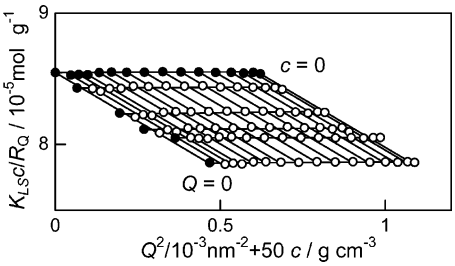

Figure 2. Zimm plot for PCHD-3 ($M_n = 11.7$ kg/mol, PDI = 1.04) in THF at 40 °C.

Table 1. $[\eta]$ and M_w from SEC On-Line with Two-Angle Light Scattering and Viscometry for PCHDs in THF and Chloroform

	THF			chloroform
	40 °C		50 °C	50 °C
sample	$M_w/10^4$	$[\eta]$ /cm^3 g^{-1}	$[\eta]$ /cm^3 g^{-1}	$[\eta]$ /cm^3 g^{-1}
PCHD-1	1.97	20.2	19.3	29.4
PCHD-2	1.77	18.8	18.4	28.5
PCHD-3	1.22	15.7	15.1	22.1
PCHD-4	0.55	11.0		13.5
PCHD-5	0.25	7.12		8.48

Table 2. Results from MALLS on PCHDs in THF

	40 °C			50 °C
sample	$M_w/10^4$	10^4A_2/ mol g^{-2}cm^3	$M_w/10^4$	10^4A_2/ mol g^{-2}cm^3
PCHD-1	1.85	-3.0	1.85	-1.7
PCHD-2	1.71	-4.0		
PCHD-3	1.17	-3.7	1.18	-2.6
PCHD-6	0.81	-4.3[a]		

[a] Measured at 30 °C.

was calculated to be 4.5 nm with the Benoit and Doty equation[17] for the wormlike chain model. This small value is consistent with the weak angular dependence observed in our light scattering data (discussed below). The Kuhn segment number $\lambda M_w/M_L$ for PCHD-1 is about 72 ± 10 in THF and 51 ± 8 in chloroform. Furthermore, the value of $[\eta]$ for each sample in THF at 50 °C is 2−5% smaller than that at 40 °C, whereas the second virial coefficient (A_2) at 50 °C is larger than that at 40 °C, as shown in Table 1. These results suggest that the excluded volume effect does not necessarily lead to a significant change on the persistence length.[12]

Light Scattering. Figure 2 is a Zimm plot for a PCHD (PCHD-3 in Table 2) in THF at 40 °C. The extrapolated infinite dilution values were almost independent of Q^2, which indicates that R_gs of the current polymer samples are too small to

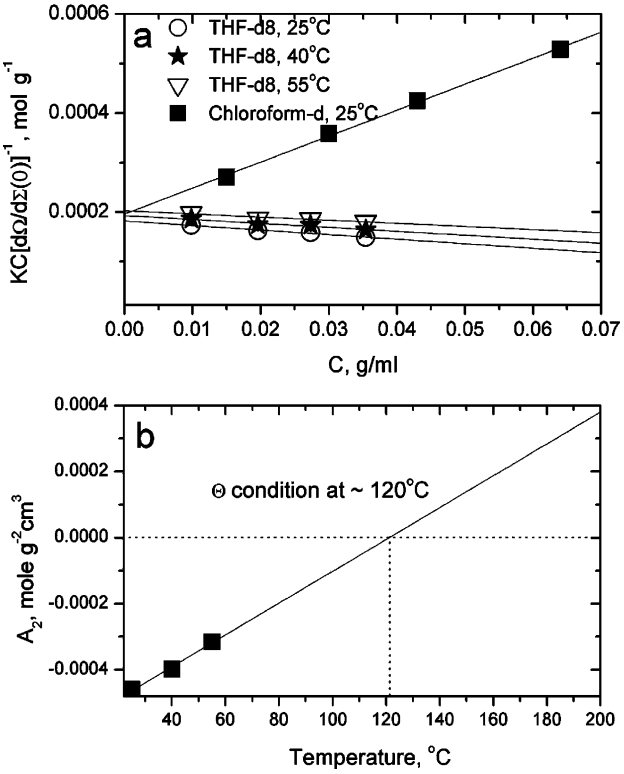

Figure 3. (a) KC dΩ/d(ΣΩ) vs C for PCHD-6 in chloroform-d at 25 °C and in THF-d_8 at 25, 40, and 55 °C. (b) A_2 variation with increasing temperature for PCHD-6.

determine by light scattering. The inverse scattering intensity at $Q = 0$ follows a straight line having a significant negative slope. M_w and A_2 thus obtained are shown in Table 2. A_2 for PCHD-1 and PCHD-3 in THF at 50 °C are appreciably larger than those at 40 °C, although still less than zero, whereas the obtained M_w is independent of temperature as expected. These results indicate that the theta temperature is higher than 50 °C. The R_g for the PCHD sample were calculated to be 23 Å in THF and 27 Å in chloroform with the Benoit and Doty equation[17,18]

$$R_g^2 = \frac{LL_p}{3} - L_p^2 + \frac{2L_p^3}{L} - \frac{2L_p^4}{L^2}\left[1 - \exp\left(-\frac{L}{L_p}\right)\right] \quad (4)$$

for the wormlike chain model with the parameters being $M_L = 200$ nm^{-1}, $\lambda^{-1} = 2L_p = 1.3$ nm, and $M = 5300$ for THF solution and $M_L = 200$ nm^{-1}, $\lambda^{-1} = 2L_p = 1.85$ nm, and $M = 5300$ for chloroform solution. These values are fairly close to those determined by SANS.

Small-Angle Neutron Scattering. For a homogeneous polymer solution the methodology to extract R_g and A_2 is well established, and R_g may be derived[10,19] via (Zimm) plots of $d\Sigma^{-1}(Q)/d\Omega$ vs Q^2.

$$\left(\frac{d\Sigma(Q)}{d\Omega}\right)^{-1} = \left(\frac{d\Sigma(0)}{d\Omega}\right)^{-1}\left[1 + \frac{Q^2R_g^2}{3} + ...\right] \quad (5)$$

M_w and A_2 may be determined from the concentration (c) dependence of $d\Sigma(0)/d\Omega$ by plotting $[d\Sigma(0)/d\Omega]^{-1}$ vs c

$$\frac{K_N c\rho^{-2}}{d\Sigma(0,c)/d\Omega} = \frac{1}{M_w} + 2A_2c \quad (6)$$

where K_N is a contrast factor which is a function of the difference

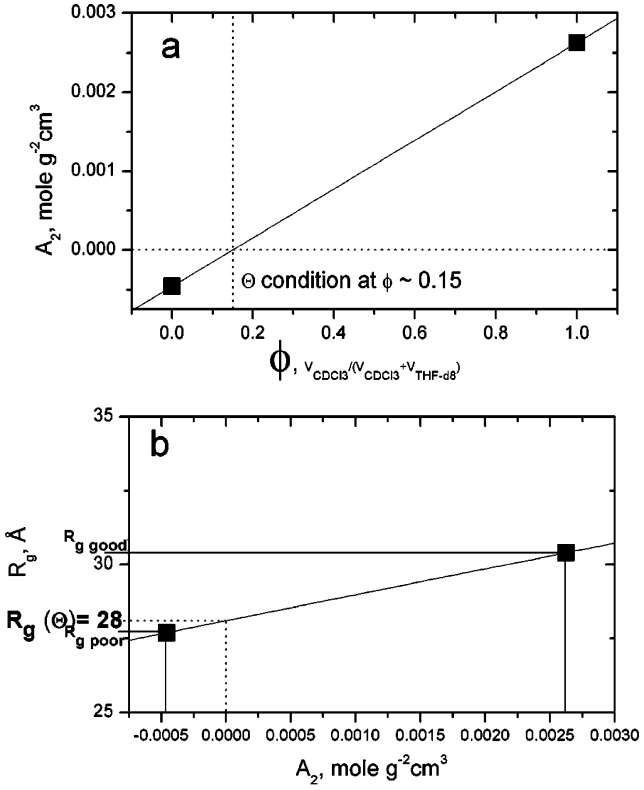

Figure 4. (a) A_2 comparison in THF-d_8 and chloroform-d (b) $R_g(C=0)$ vs A_2.

in scattering power between the solute molecules and the solvent

$$K_N = \frac{N_A}{\rho^2}\left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 \qquad (7)$$

N_A is Avogadro's number and b_i and v_i are the scattering length and specific volume of a monomer of polymer i, respectively, and ρ is the density (1.07 g/mL for PCHD).[10,19−21]

After subtracting incoherent backgrounds, SANS data from a PCHD (PCHD-6 in Table 2) in THF-d_8 at 25 °C are shown in Figure 3 as a function of polymer concentration and were fitted via Zimm plots (eq 6) and also to the Debye function (eq 8) to determine $d\Sigma(0)/d\Omega$ with good agreement (±5%) between the two approaches.

$$P(Q) = (2/Q^4R_g^4)[\exp(-Q^2R_g^2) - 1 + Q^2R_g^2] \qquad (8)$$

The measured radii at several concentration were extrapolated to $C = 0$ to obtain $R_g(C=0)$. The M_w and A_2 values were determined from eq 6.[10,19] Typical plots of $KC[d\Sigma/d\Sigma(0)]^{-1}$ vs C for a PCHD (PCHD-6 in Table 2) in two different solvents are shown in Figure 3a. The A_2 values for PCHD-6 in chloroform-d are positive (Figure 3a), indicating good solvent condition, while the A_2 values in THF-d_8 are negative at all temperatures, showing poor solvent quality. However, compared to the large positive slope in chloroform-d, the polymer in THF-d_8 is close to the Θ condition. The temperature variation of A_2 (Figure 3b) suggests that the Θ condition ($A_2 = 0$) for this polymer−solvent system might be around 120 °C, which is above the boiling point (~65 °C) of THF-d_8, and this is consistent with the light scattering results. The values of A_2 for PCHD-6 in mixed solvents (THF-d_8 + chloroform-d) at 25 °C are shown in Figure 4a. These data suggest that a mixed solvent with $\phi_{CDCl_3} \sim 0.15$ may be close to the Θ conditions for PCHD-6 at 25 °C. The plot of $R_g(C=0)$ vs A_2 for PCHD-6 suggests that R_g at the Θ condition is 28 Å for this particular molecule (Figure 4b).

In summary, we report here the solution properties of PCHD in THF and chloroform derived from neutron scattering, light scattering, and viscometry studies. All the results indicate that PCHD (high 1,4/1,2 ratios) is not as stiff as initially suggested. However, these molecules are unlike common flexible coil vinyl polymers such as polystyrene. Specifically, the Kuhn segment length of PCHD having high 1,4 microstructure is similar to that of polystyrene, while the bead diameter of PCHD is much smaller.

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