Optical Anisotropy as an Index of Polymer Microstructure in Poly(phenylmethylsiloxane) Chains

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ABSTRACT: Absolute depolarized intensity R_{VH} for newly synthesized poly(phenylmethylsiloxane) (PPMS) chains with different stereochemical structure has been obtained from the low-frequency depolarized Rayleigh spectra of dilute PPMS solutions in CCl_4 at 25 °C. The effective optical anisotropy $\langle\gamma^2\rangle/x$ of PPMS with degree of polymerization $x \approx 160$ was found to be insensitive to refractive index variation with different solvents. The measured optical anisotropy of the monomer $\langle\gamma^2\rangle$ and polymer were compared with computed values based on the rotational isomeric state theory. In the latter, geometry of the chain, conformational energies, and group anisotropies were obtained from the analysis of the experimental molar Kerr constant ${}_mK$ and optical configuration parameter $\Delta\alpha$ for atactic PPMS. The theoretical calculation of $\langle\gamma^2\rangle/x$ yields a good qualitative account of its main feature, i.e., insensitivity to x (for $x > 60$) and variation with chain tacticity. The theoretical value, however, exceeds the experimental $\langle\gamma^2\rangle/x$ while agreement is achieved with the experimental ${}_mK$ and $\Delta\alpha$. Better approximation of γ^2 and $\langle\gamma^2\rangle/x$ requires modification of the conformational energies and a lower value for the group anisotropy $\Delta\alpha_{SiPh}$, whose magnitude is quite uncertain. Possible explanations for this discrepancy are discussed herein.

Introduction

Among the scattering techniques, depolarized Rayleigh scattering is a valuable tool for probing fluctuations in the anisotropic part $\hat{\alpha}$ of the polarizability tensor. For polymer chains composed of optically anisotropic repeat units both the configurational average optical anisotropy $\langle\gamma^2\rangle$ and the relaxation times for segmental and overall orientation can be obtained from the depolarized Rayleigh spectrum $I_{VH}(\omega)$.[1-4]

The integrated intensity of the $I_{VH}(\omega)$ spectrum, measured with a Fabry-Perot interferometer of suitable free spectral range, yields the intrinsic optical anisotropy $\langle\gamma^2\rangle$ assuming the validity of the second-power spherical Lorentz local field approximation.[5] The high-frequency component of the collision-induced anisotropy appears as a nonzero background. Absolute depolarized light scattering measurements were previously performed without the use of a Fabry-Perot interferometer by using a set of narrow band interference filters of different widths and correction factors in order to extract the contribution of the intrinsic optical anisotropy only.[5] The collisional scattering can also be removed by recording the Rayleigh wing of the depolarized Raman scattering on a grating monochromator.[6,7] However, due to stray light only the spectral region greater than a few reciprocal centimeters was recorded and moreover a spectral decomposition of the total $I_{VH}(\omega)$ to its components is needed.

The optical anisotropy $\langle\gamma^2\rangle$ is usually treated as a constitutive property and as such it can be a sensitive index of chain conformation and microstructure. In fact the main objective of the present investigation is to examine the applicability of the depolarized Rayleigh spectroscopy to probe variations in the chain microstructure. For this purpose, we use poly(phenylmethylsiloxane) (PPMS) samples with different stereochemical structures, which were recently synthesized. Rotational isomeric state (RIS) calculations of the unperturbed chain dimensions $\langle r^2\rangle_0$ have shown that the manifestation of the stereochemical microstructure is different in PPMS than in polystyrene (PS).[8] RIS model calculations of $\langle\gamma^2\rangle$, which have already been reported for PS,[9] are also carried out for PPMS to compare with the experimental values.

Experimental Section

The depolarized Rayleigh spectra of the PPMS solutions in CCl_4 were taken at a scattering angle of 90° by using a plane Fabry-Perot interferometer with a free spectral range of 40 cm^{-1}. The polarizers used for the incident and scattered light have extinction coefficients better than 10^{-6} and 10^{-7}, respectively. The experimental spectra of the solvent CCl_4, of PPMS ($M_w = 2.17 \times 10^4$), and of neat benzene used as a standard at 25 °C are shown in Figure 1. The free spectral range of the interferometer permit separation of the spectral component due to the intrinsic anisotropy from the high-frequency component of the collision-induced scattering resulting in a nonzero background. The observed low-frequency $I_{VH}(\omega)$ for the isotropic CCl_4 is assigned to intermolecular transient anisotropy due to short-range interactions between pairs of molecules and nonvanishing molecular anisotropy of CCl_4 molecules in assymetric low vibrational states.[10] The orientational motion of liquid CCl_4 has recently been observed by hyper-Rayleigh light scattering.[11] Integrated depolarized intensities for the narrow spectra were obtained from numerical integration. On the other hand, the broad spectra of the solvents used were represented by a single Lorentzian taking into account the overlap of neighboring orders.

The depolarized intensity attributed to the solute molecules with volume fraction Φ, i.e., $I_{VH} = I_{solu} - (1 - \Phi)I_{solv}$, is calculated from the measured intensities of the solution and the inert neat solvents. The I_{VH} intensity is then converted to the absolute Rayleigh's ratio, R_{VH}, by comparison with the depolarized Rayleigh ratio $R^B{}_{VH}$ of benzene according to

$$R_{VH} = (I/I_B)(n/n_B)^2 R^B{}_{VH} \quad (1)$$

The $R^B{}_{VH}$ at $\lambda = 488$ nm and 25 °C amounts to 2.67×10^{-6} cm^{-1}.[12] Refractive indices n of the samples were measured with an Abbé refractometer.

The poly(phenylmethylsiloxane) (PPMS) samples were very recently prepared by an anionic ring-opening polymerization of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane. The full procedure and sample characterization is described elsewhere.[13]

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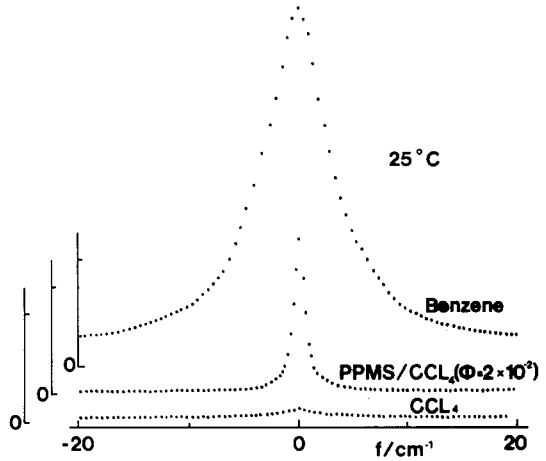

Figure 1. Depolarized Rayleigh spectra of poly(phenylmethylsiloxane) (M_n = 2.17 × 10^4) in CCl_4, neat CCl_4, and neat benzene at 25 °C.

Table I
Molecular Characteristics, Depolarized Rayleigh Intensities, and Optical Anisotropies of PMMS Samples

sample	$M_n \times 10^{-4}$, g/mol	W_m	R_{VH}/ρ, 10^{-28} cm²	$\langle\gamma^2\rangle/x$, Å⁶
PPMS ≠ 10	2.17	0.449	8.3	23.8 ± 0.5
PPMS ≠ 4	2.24	0.569	7.5	21.3 ± 0.6
PPMS ≠ 8	8.42	0.67	6.8	19.6 ± 0.8
PPMS ≠ 12	1.87	0.749	8.5	24.3 ± 0.8
PMS[a]			6.8	19.1 ± 0.9
dimer[b]			8.5	22.6
PS	35.0	0.5	13.2	38 ± 1

[a] Dimethoxyphenylmethylsilane.[2] [b] Reference 2.

The percentage of isotactic (mm), heterotactic (mr), and syndiotactic (rr) triads was obtained from the corresponding 400-MHz ^{1}H NMR peaks according to Baratova's assignment.[14] The percentage of meso diads $W_m = (2W_{mm} + W_{mr})/2$ along with the molecular weight obtained from viscosity measurements is given in Table I. The assignment of the ^{1}H NMR peaks according to Llorente et al.[15] would result to $W'_m = 1 - W_m$. The sample with the highest W_m, i.e., more isotactic, was found to be partially crystalline. Dust-free samples were obtained after filtration through 0.5-μm Teflon Millipore filters directly into the dust-free rectangular (1 × 1 cm) Hellma cells.

Results

The effective mean-square optical anisotropy $\langle\gamma^2\rangle/x$ per monomer unit can be computed from

$$\langle\gamma^2\rangle/x = 15(\lambda_0/2\pi)^4 f(n)^{-1}(R_{VH}/\rho) \quad (2)$$

where x is the degree of polymerization, λ_0 the wavelength of light in vacuo, ρ the number density of monomer units, and $f(n) = ((n^2 + 2)/3)^2$ the second-power spherical Lorentz local-field correction. The exact form of the local field and its power are still points of contraversy.[16,17] The solvent can affect the solute anisotropy either by introducing a "form" anisotropy or by anisotropic dipole-induced–dipole solute–solvent interactions[16] not accounted for by a spherical dielectric cavity. The former contribution should depend on the solute molecular weight and the refractive index of the solvent.[4,19] This "shape" anisotropy is generally small.[18] Recent optical anisotropy measurements on polyisoprene with different molecular weights show no evidence for a contribution from shape anisotropy.[3] On the other hand, a quantitative account for the anisotropic nature of the local field would require either detailed knowledge of molecular pair distribution functions[16] or application of ellipsoidal Lorentz or Onsager-Scholte internal fields with unknown shape

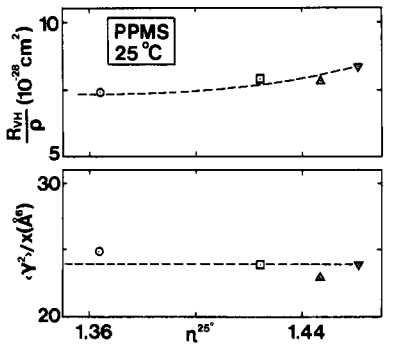

Figure 2. Depolarized Rayleigh ratio and optical anisotropy of PPMS solutions (M_n = 2.17 × 10^4) in different solvents plotted versus their refractive indices at 25 °C (⊙, acetone; ⊡, dioxane; ▲, $CHCl_3$; ▼, CCl_4).

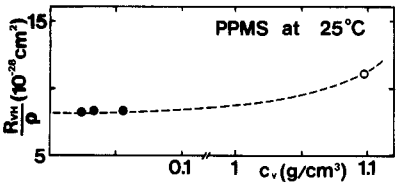

Figure 3. Absolute ratio R_{VH}/ρ of PPMS (M_n = 2.17 × 10^4) in CCl_4 versus solute concentration at 25 °C (●, dilute solutions; O, bulk).

and distance parameters and elements of the solute polarizability tensor as well.[19,20] This ill-conditioned problem has probably caused the persistence of the second-power Lorentz internal field correction for the depolarized Rayleigh intensity[2,17] and consequently for the optical configuration parameter $\Delta\alpha$ and molar Kerr constant.[21]

To check for the full substraction of the collision-induced depolarized scattering and examine the effect of the refractive index on the computed $\langle\gamma^2\rangle$, we have measured the I_{VH} of PPMS (M_n = 2.17 × 10^4) solutions in different solvents. Figure 2 shows that while R_{VH}/ρ increases with increasing n, the optical anisotropy is insensitive to the variation of n. This behavior, which is expected for a spherically symmetric cavity, can also be the result of cancellation of several corrections to the local field factor. Nevertheless, the results of Figure 2 allow the determination of a solvent-independent molecular anisotropy $\langle\gamma^2\rangle$ for PPMS to be compared with subsequent theoretical calculations.

The absolute R_{VH} intensity was also measured at different solute concentrations to verify the presence of appreciable intermolecular orientation correlations in $\langle\gamma^2\rangle/x$. The concentration dependence of R_{VH}/ρ is depicted in Figure 3 for PPMS (M_n = 2.17 × 10^4) solutions in CCl_4 at 25 °C. The $\langle\gamma^2\rangle/x$ is insensitive to concentration variations in the considered dilute range.[2] The values of $\langle\gamma^2\rangle/x$ thus calculated are listed in Table I together with the optical anisotropy used to estimate the depolarized light scattering from the repeating unit in PPMS. For comparison the experimental $\langle\gamma^2\rangle/x$ of an atatic PS (M_w = 3.5 × 10^5) is also given in Table I. The RIS result for α-PS is reported to be 33 Å.[6]

Theoretical Calculations

Values of $\langle\gamma^2\rangle/x$ for chains with degrees of polymerization up to x = 100 were computed according to standard methods of matrix multiplication.[21,22] Values shown below for heterotactic samples (i.e., $0 < W_m < 1$) are averages over 20 independently generated Monte Carlo chains with Bernoullian placement of meso and racemic diads. Exploratory calculations proved that $\langle\gamma^2\rangle/x$ increases with

x reaching asymptotic limits at $x \approx 60$ with typical differences between the results computed for $x = 60$ and $x = 100$ on the order of 1–2%. All the values shown below were computed with $x = 100$.

Geometry of the chain, conformational energies, and optical parameters were taken from previous publications.[8,15,23-26] In brief, valence angles $\theta = 143.0°$ and 109.5° were used for skeletal bonds meeting at the O and Si atoms, respectively. Rotational isomers were placed at the perfectly staggered position 0,±120°. Dipole moments of ±0.6 D and bond lengths of 1.64 Å were used for skeletal SiO bonds. Conformational energies, in kcal/mol, are $E_\sigma = 0.35$, $E_\omega = 1.6$; $E_{\omega'} = -2.5$, $E_{\omega''} = -0.9$, $E_{\omega'''} = -0.5$, and $E_\delta = -1.0$. Finally, the optical anisotropies required to formulate the traceless tensor $\hat{\alpha}$ for the repeating unit are $\Delta\alpha_{SiPh} = 5.1$, $\Delta\alpha^+_{SiPh} = -3.0$, $\Delta\alpha_{SiO} = 1.3$, and $\Delta\alpha_{SiCH_3} = 1.25$, all in Å^3.

Values of conformational energies and optical parameters quoted above will be referred to as the "main set". They were assigned by critical analysis of the results of the optical configuration parameter[15] $\Delta\alpha$ and the molar Kerr constant[23] ${}_mK$ of this polymer. Experimental values of these magnitudes are $\Delta\alpha = -12.1$ Å^3 (unswollen sample) and −8.5 Å^3 (sample swollen with decalin) at 25 °C for PPMS with $W_m = 0.5$, and ${}_mK = 1.9 \pm 0.5 \times 10^{-25}$ m^5 V^{-2} mol^{-1} at 21 °C for PPMS with $W_m = 0.5$ using p-dioxane as solvent. It is worth mentioning that the same internal optical field factor was used for their calculation.

The values of $\langle\gamma^2\rangle/x$ computed with the main set of parameters are shown as a function of W_m in line a of Figure 4. For the repeating unit ($x = 1$), $\gamma^2 = 21.1$ Å^6 is obtained with this set, while the results of $\Delta\alpha$ and ${}_mK$ are −12.6 Å^3 and 1.6×10^{-25} m^5 V^{-2} mol^{-1}, respectively. Therefore, the main set gives good account of $\Delta\alpha$ and ${}_mK$ of this polymer (in fact, this set was assigned to do exactly this); however, it tends to overestimate the values of γ^2. In the case of the repeating unit, the discrepancy between theory and experiment is ca. 10%, but for the polymer, theoretical values of $\langle\gamma^2\rangle/x$ are roughly twice the experimental results.

The magnitude $\langle\gamma^2\rangle/x$ is quite sensitive to some of the parameters used on the calculation. Thus, it increases with increasing E_σ, E_δ, or $\Delta\alpha_{SiPh}$ and decreases when $\Delta\alpha_{SiO}$ increases. Consequently, is is rather easy to lower the calculated values into agreement with experiment; it is enough to either decrease $\Delta\alpha_{SiPh}$ by ca. 1.3 Å^3 or to increase $\Delta\alpha_{SiO}$ by ca. 1.0 Å^3 to bring agreement between theory and experiment. The problem is that any of these modifications worsens the agreement for the other three experimental magnitudes, namely, γ^2 of the repeating unit and $\Delta\alpha$ and ${}_mK$ of the polymer.

We have tried to optimize the parameters in order to reach the best possible simultaneous fitting for these magnitudes. The optimization procedure that we have used consisted of two steps: First, the optical parameters were adjusted until they exactly reproduce the experimental value of γ^2 for the repeating unit, which does not depend on any conformational energy. Once these parameters were chosen, the energies were adjusted in order to obtain the best possible agreement for $\langle\gamma^2\rangle/x$, $\Delta\alpha$, and ${}_mK$ of the polymer.

Figure 5 shows the variation of γ^2 of the repeating unit with the four anisotropies. The value of $\Delta\alpha_{SiCH_3}$ is almost irrelevant; however, the other three anisotropies have a large effect on the result of γ^2. If only one of the parameters is modified, the experimental value can be reproduced by using $\Delta\alpha_{SiPh} = 4.8$, $\Delta\alpha^+_{SiPh} = -2.5$, or $\Delta\alpha_{SiO} =$ 1.5 Å^3. Of course, any equivalent combination of modifications of two or three of the parameters can also be used. Exploratory calculations were carried out with several sets of parameters that reproduce γ^2 of the repeating unit, and all of them gave almost the same results for the polymer. In all the calculations presented below, the combination $\Delta\alpha_{SiPh} = 4.9$, $\Delta\alpha^+_{SiPh} = -2.9$, $\Delta\alpha_{SiO} = 1.3$, $\Delta\alpha_{SiCH_3} = 1.25$ was used. Thus, the modifications are introduced in the parameters representing the phenyl group on which the additivity of tensors is most likely to fail due to delocalization of the electrons.

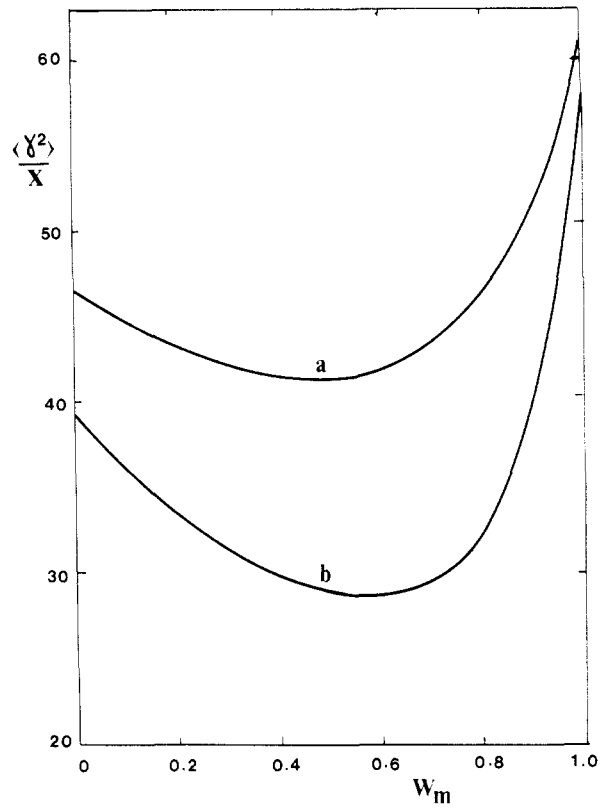

Figure 4. Variation of the mean optical anisotropy per repeating unit $\langle\gamma^2\rangle/x$ with the tacticity of the polymer W_m, computed at 25 °C for chains of $x = 100$ repeating units. Values shown for heterotactic samples (i.e., $0 < W_m < 1$) are averages over 20 independently generated Monte Carlo chains; standard errors of these averages are roughly represented by the thickness of the lines. Line a: main set of parameters. Line b: $\Delta\alpha^+_{SiPh} = -2.9$, $\Delta\alpha_{SiO} = 1.3$, $\Delta\alpha_{SiCH_3} = 1.25$, $E_{\omega''} = 0$, and $E_\delta = -1.7$.

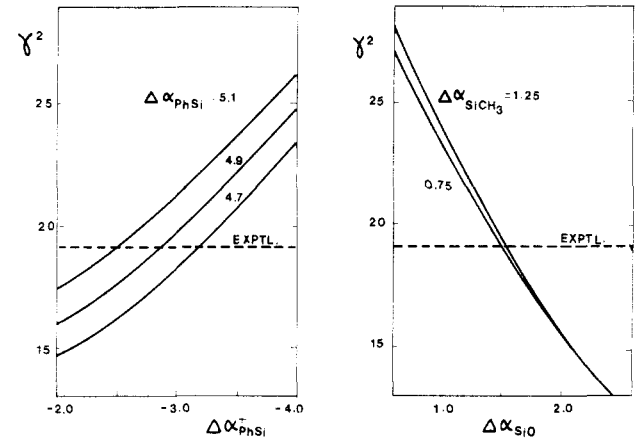

Figure 5. Variation of the optical anisotropy of the repeating unit γ^2 with the optical parameters.

The most effective way of lowering the theoretical values of $\langle\gamma^2\rangle/x$ is to decrease the energy E_δ. Unfortunately, agreement with experience requires the use of $E_\delta \approx -2.1$ kcal/mol, for which theoretical values of both $\Delta\alpha$ and ${}_mK$ are smaller than the experimental ones. A reasonable compromise for the three magnitudes can be obtained with a simultaneous adjustment of both E_δ and $E_{\omega''}$. Both energies represent second-order interactions of the phenyl ring (with the CH_3 group in the case of $E_{\omega''}$ and with the O atom for E_δ) and therefore their values are not particularly accurate. Thus, taking $E_{\omega''} = 0$ and $E_\delta = -1.7$ kcal/mol, values of $\Delta\alpha = -10.7$ Å^3 and ${}_mK = 1.5 \times 10^{-25}$ m^5 V^{-2} mol^{-1} are obtained.

The value of $\Delta\alpha$ is roughly in the middle of the experimental results obtained for unswollen and swollen samples, while ${}_mK$ is still within the limits of experimental error for this magnitude. Values of $\langle\gamma^2\rangle/x$ obtained with $E_{\omega''} = 0$, $E_\delta = -1.7$ kcal/mol are shown as a function of W_m in line b of Figure 4. Although theoretical results are still larger than experimental, differences are much smaller than those obtained with the main set, and on the other hand, the shape of the variation of $\langle\gamma^2\rangle/x$ with W_m is very similar to that obtained in the Experimental Section, with a minimum at $W_m \approx 0.6$–0.7. The sharp increase of $\langle\gamma^2\rangle/x$ for highly isotactic polymers ($W_m \approx 1$) is due to the predominance in the meso diad of the tt conformation, which produces extended, and therefore anisotropic, chains. In the case of syndiotactic polymers ($W_m \approx 0$), the preferred conformations are tg^- and g^-t, which generate helices and therefore also increase the value of $\langle\gamma^2\rangle/x$.

We can conclude that the theoretical calculation of $\langle\gamma^2\rangle/x$ for PPMS gives good qualitative account of the main features of this magnitude, like its insensitivity to x at $x > 60$ and the variation with tacticity. However, if standard values of the parameters are used, theoretical values are much larger than experimental results. To improve the agreement with experiment requires modifications of almost 1 kcal/mol in some of the conformational energies and implies a worse agreement for other conformation-dependent properties like $\Delta\alpha$ and ${}_mK$.

An alternative explanation for the failure of quantitave comparisons would be to assume that the optical parameters $\Delta\alpha$ are not exclusively determined by the chemical nature of the polymer, but instead they depend on the environment of the chain. This kind of dependence has been postulated several times as responsible for the disagreement between theoretical and experimental values of $\Delta\alpha$ for many polymers. Up to now there has been no attempt to incorporate any modifications of the $\Delta\alpha$'s by either the physical state of the polymer or the solvent into the scheme of the calculation. However, if we assume just as a hypothesis that the solvent can modify the optical parameters of the chain, it is conceivable that a symmetrical solvent, like CCl_4, could decrease the anisotropy of the polymer units. Thus, theoretical values of γ^2 computed with standard sets of $\Delta\alpha$'s will overestimate the results for a single repeating unit and even more severely for a whole chain for which the modification of parameters could be much larger. However, this conjecture is not along the line of the data of Figure 2. On the other hand, the optical configuration parameter shows a large decrease upon swelling with decalin, which cannot be accounted for only by weak positive intermolecular correlations,[2] but instead nice agreement can be achieved by decreasing the mostly uncertain value $\Delta\alpha_{SiPh}$.[15] Conversely, if collisional effects (and hyperpolarizabilities) contribute to the optical Kerr effect,[27,28] then the reported ${}_mK$ is likely to exceed its intrinsic value. Finally, corrections for the small dispersion in the polarizability anisotropies[29] due to the different wavelengths (488, 632.8 nm) used would not improve the differences.

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