Polyphosphazenes with High Refractive Indices: Optical Dispersion and Molar Refractivity

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ABSTRACT: The optical properties of a series of high refractive index polyphosphazenes were investigated. The wavelength-dependent change in refractive index (optical dispersion) associated with two selected polymers was examined using variable-angle spectroscopic ellipsometry. Values of the Abbé number for these polymers were calculated. These systems have a $\nu_D = 20-25$, which compares closely with other organic polymers with similar refractive indices. Calculation of the molar refractivity (R_m) associated with the [N═P] repeat unit structure yielded a value of R_m[N═P] = 14.36 cm^3/mol. This value is compared with other polymer repeat unit structures. The comparison indicates that the [N═P] repeat unit has a linear polarizability close to that found in conjugated [C═C] bonds.

Introduction

Optical Properties. The optical properties of materials are becoming increasingly important as advances continue toward the development of practical photonics.[1−3] In this field, optical properties such as dispersion, absorption, and polarization are considered to be three of the most important features of a glassy solid. Materials that have high refractive indices are of special value for use in photonics.[3] Unfortunately, most of the high refractive index materials available for optical applications are inorganic-based glasses which are heavy and brittle and may be expensive. Organic polymers of optical quality have been considered as alternatives to the inorganic glasses.[4−6] They offer the advantages of lightness of weight, toughness, and ease of fabrication. In addition, polymers can be designed and synthesized to have a variety of physical property combinations that are not possible for inorganic glasses. However, a major drawback of typical organic polymers is their relatively low refractive indices ($n = 1.3-1.7$).

Many high refractive index polymers have been reported.[4−22] These systems usually consist of highly conjugated, aromatic-type, π-electron systems that bear heavy elements such as bromine or iodine.[4−6,8,18−22] However, such polymers give very high optical dispersions. Highly conjugated polymers also tend to be insoluble and absorb strongly in the visible region of the spectrum.[5,14,23,24]

The optical dispersion gives an indication of the bandwidth over which a material is optically useful.[1−3] A value of the optical dispersion can be obtained through measurement of the Abbé number (ν_D) of a material

$$\nu_D = \frac{n_D - 1}{n_F - n_C}$$

where n_F, n_C, and n_D are the refractive indices at λ = 486, 656, and 589 nm. Typically, organic polymers with values of $n = 1.7$ or higher will have an Abbé number $\nu_D < 20$, compared with $\nu_D > 50$ for inorganic systems.[14] This indicates a substantial change in the refractive index over the visible spectrum. A few organic polyelectrolyte systems, which have a metal−polymer salt-like structure, have been shown to have both high refractive indices and low optical dispersions (high Abbé numbers).[7]

The refractive index of a polymer is a measure of an average property of the material in its aggregated state, and the molecular weight and density of the polymer influence the overall value of the refractive index.[25] An effective assessment of the contributions from the constituent chemical groups to the refractive index of a polymer can be obtained through a determination of the molar refractivity.[26,27] The measurement of this quality provides a good means for correlating the molecular structure of a system with the optical properties.[25−27] According to Denbigh and Stein, the molar refractivity (R) can be assumed to be an additive function arising from the sum of the individual refractions (R_i) from all the bonds that make up the polymer ($R = \sum R_i$).[28,29] For the case of a homopolymer, the molar refractivity is given by $R = (DP)R_m$, where DP is the degree of polymerization and R_m is the monomer repeat unit molar refractivity.[25] The value DP can be obtained quite easily if the molecular weights of both the polymer (M) and the repeat unit (M_m) are known, because DP = M/M_m. This can be considered with the Lorentz−Lorenz equation to give

$$R_m = \frac{n^2 - 1}{n^2 + 2}\left(\frac{M_m}{\rho}\right)$$

where ρ is the density and n is the refractive index.[30]

The molar bond contributions for many chemical units have been tabulated and are readily available.[31] This makes it possible to calculate the molar refractivity values for a wide range of repeat unit structures of both nonconjugated and (recently) conjugated organic polymers and to predict the refractive indices (n) of a variety of polymer systems.[32] Such values have been compared with experimentally determined values of n for a number of different polymer systems, and they have been found to be accurate to within 1%.[31]

Polyphosphazenes. Polyphosphazenes are a broad class of polymers (well over 700 different structures are known to date) which have a wide range of properties that vary according to the nature of the side groups.[33,34]

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It would be useful to be able to predict the refractive index values of various polymers within this system. The Lorentz−Lorenz equation can be applied to single-substituent polyphosphazenes since the repeat unit is consistent and has the structure [N=PR_2]. However, no comprehensive data are currently available about the molar refractivity contribution from the [P=N] bond. This is important from both the fundamental and applied viewpoints. Although polyphosphazenes are depicted as having a backbone of alternating single−double bonds, no firm evidence exists that this structure is a conjugated bonding arrangement.[35] It has been suggested that the phosphazene structure is allylic or even zwitterionic in nature, and it would be worthwhile to compare the molar refractivity value of the [P=N] unit with the molar refractivity value of other polymer repeat units.

Many reasons exist why polyphosphazenes are of interest for optical applications. Polyphosphazenes have an inorganic P−N backbone and offer the potential to be high refractive index materials because of their increased electron density relative to saturated carbon backbone polymers.[33,36−38] It has been shown that, with the appropriate choice of side-group structures, polyphosphazenes with high refractive index values (n = 1.6−1.75) can be synthesized.[39,40] In addition, the inorganic nature of the backbone structure confers an increased thermooxidative and photolytic stability to these systems.[34,41] The macromolecular substitution approach usually employed for the synthesis of these polymers allows the preparation of multiple side-group structures that are difficult or impossible to prepare for organic backbone polymers.[34,41] Such systems could be of considerable value in the development of photonic materials.[1−3]

In this work, a series of different polyphosphazenes has been investigated, and calculations were made to obtain the molar refractivity contributions of the [N=P] repeat unit. Two polymers were selected from this series and were investigated through spectroscopic ellipsometry. This was done in order to obtain information about the optical dispersion of polyphosphazenes and for comparison with other polymer systems.

Results and Discussion

Nine polymers were investigated in this work. These consisted of three sets: the phenoxy (**1**−**3**), naphthoxy (**4**−**6**), and the naphthoxyethoxy (**7**−**9**) side-group-containing polymers. Within each series of polymers, the side groups contained hydrogen, bromine, or iodine atoms. The polymer structures are depicted in Chart 1. These polymers were synthesized previously, and the details of their preparation and characterization have been reported.[40]

Optical Dispersion. Spectroscopic ellipsometry was used to obtain information about the optical dispersion associated with polyphosphazenes. Measurements were obtained on only one set of polymers, the naphthoxy-ethoxy-based set. Within this group of polymers, data could be acquired only for polymers **7** and **8**. Polymer **9** was insoluble in all solvents that were suitable for the spin-coating procedures employed, and optical quality thin films could not be obtained.

The wavelength-dependent refractive index data, $n(\lambda)$, were acquired from transparent, isotropic, thin films spun cast on silicon wafers. The transmission data, $k(\lambda)$, were determined from transparent, thin films spun cast on quartz disks. Both $n(\lambda)$ and $k(\lambda)$ were plotted, and

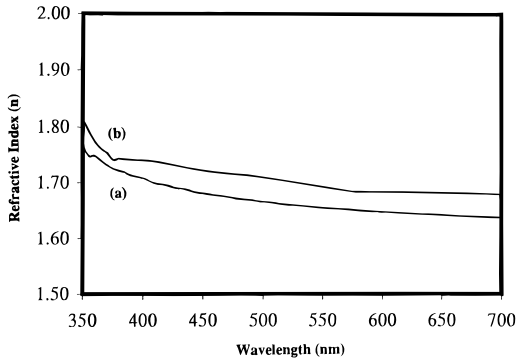


Figure 1. Wavelength dependence of the refractive index for polymers (a) [$NP(OCH_2CH_2O(C_{10}H_8))_2]_n$ and (b) [$NP(OCH_2CH_2O(C_{10}H_7Br))_2]_n$.

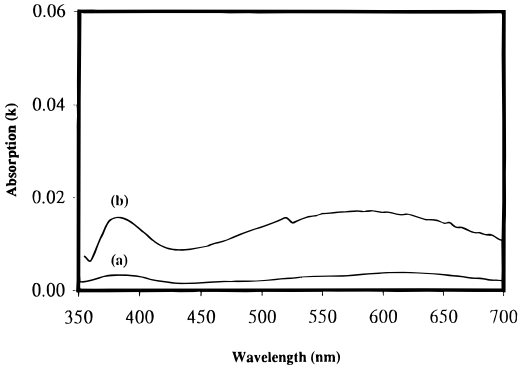
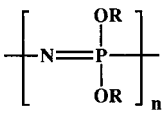
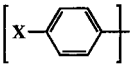
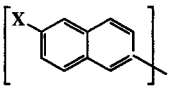
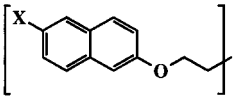


Figure 2. Transmission data for polymers (a) [$NP(OCH_2CH_2O(C_{10}H_8))_2]_n$ and (b) [$NP(OCH_2CH_2O(C_{10}H_7Br))_2]_n$.

Chart 1



R	X = H	Br	I
	1	2	3
	4	5	6
	7	8	9

the results are shown in Figures 1 and 2. The refractive index values obtained for polymer **8** were consistently higher (over all λ values) than the values obtained for polymer **7**. This was expected because the electron density of the side groups in polymer **8** was higher than the electron density of the corresponding groups in polymer **7**. Accordingly, polymer **9** would be expected to have an even higher refractive index (over all λ), but this could not be verified.

The values of the refractive index obtained for polymers **7** and **8** (at 550 nm) by ellipsometric measurement were slightly higher than those obtained for the same polymers using the immersion oil technique.[31,42] The immersion oil technique gave values of n = 1.634 for polymer **7** and n = 1.648 for polymer **8**, compared with

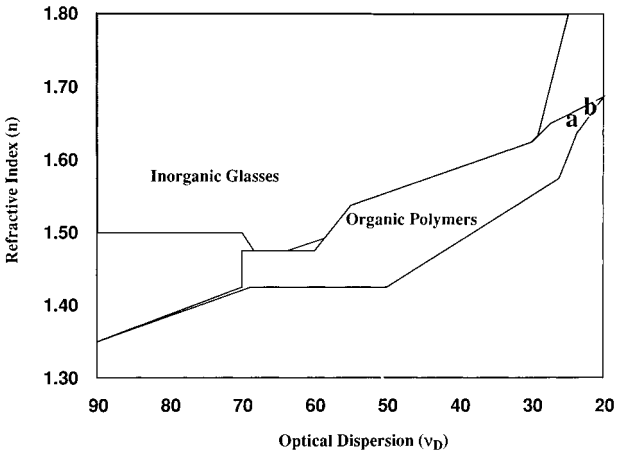


Figure 3. Comparison of polymer optical properties (after Dislich[23]): (a) $[NP(OCH_2CH_2O(C_{10}H_8))_2]_n$; (b) $[NP(OCH_2CH_2O(C_{10}H_7Br))_2]_n$.

values of $n = 1.655$ and 1.675 as determined by ellipsometry. This is understandable, since the immersion oil method relies on a significant component of empirical judgment and is more susceptible to experimental error.[42] However, the agreement between these two methods was within 2%, and this indicates that the immersion oil method is sufficiently accurate to be used for rough estimates of the refractive index values.

The Abbé numbers for polymers **7** and **8** were calculated using the refractive index data obtained through ellipsometry, at 589, 486, and 656 nm. Calculations yielded $\nu_D = 24.16$ for polymer **7** and $\nu_D = 21.52$ for polymer **8**. These numbers are similar to dispersion values obtained for organic-based, conjugated, high refractive index polymers.[32] The n_D versus ν_D values obtained for polymers **7** and **8** were plotted relative to inorganic glasses and other organic-based polymer systems (Figure 3) according to Dislich.[14,23]

Molar Refractivity. The experimentally determined values of R_m for the repeat unit structures of polymers **1**−**9** were determined with the Lorentz−Lorenz equation, using the refractive indices obtained for these polymers by the immersion oil method.[40] These refractive index values were used because ellipsometric refractive index values were not available for all nine polymers. However, an underestimation of the molar refractivity is expected with use of these values since, as discussed, the immersion oil technique appears on average to give lower refractive index values than those given by ellipsometry. The refractive index values were obtained at 550 nm, which is the maximum emission wavelength for the tungsten light source used. The molar refractivity of the repeat unit was then estimated from an additive combination of the tabulated Lorentz−Lorenz values for the distinct chemical group contributions of the repeat unit structures plus a R_m[P═N] term. Based on the optical dispersion exhibited by these polymers, the variations of the refractive index values between 550 and 589 nm were considered small enough to allow the use of the molar group contribution values at 589 nm.[31,42] The difference between the estimated R_m for the repeat unit structure and the experimental R_m yielded the value for R_m[P═N]. These results are listed in Table 1. A statistical treatment using the Q-test and standard error analysis was conducted to reject any spurious data.[43] From the analysis of the relevant data, a value of R_m[P═N] of 14.36 ± 1.27 cm^3/mol was obtained.

Table 1. Molar Refractivity and Associated Data for Polymers[a]

polymer	ρ (g/cm^3)	n (550 nm)	[A] (g/mol)	R_m[A]	$*R_m$[P═N]
1	1.18	1.620	231.0	68.77	13.89
2	1.65	1.646	389.0	85.57	15.31
3	1.96	1.715	483.0	96.81	16.25
4	1.24	1.664	331.0	99.04	12.40
5	1.69	1.688	489.0	110.35	15.30
6	1.82	1.755	583.0	131.16	12.98
7	1.22	1.634	419.0	122.81	14.31
8	1.55	1.648	577.0	135.44	18.55
9	1.65	1.684	671.0	154.38	14.44

[a] [A] is the repeat unit structure for the polymer. Molar refractivity values are at 550 nm, in cm^3/mol.

A comparison can be made of R_m[P═N] to other repeat unit structures in order to gauge the polarizability of the phosphazene [P═N] electrons. A phenylene [C_6H_4] repeat unit structure has $R_m = 25.03$ cm^3/mol, a nonconjugated [C═C] structure has $R_m = 8.88$ cm^3/mol, and a polysulfur [S−S] repeat unit has $R_m = 16.17$ cm^3/mol. Unfortunately, the conjugated R_m[C═C] value was not available at $\lambda = 589$ nm. At $\lambda = 700$ nm this has a value of 16.95 cm^3/mol. A comparison to nitrogen-containing units is also of interest. The nitrile [C≡N] group has $R_m = 5.53$ cm^3/mol, and a tertiary amine [3°-(N)] group has $R_m = 2.80$ cm^3/mol.

It is evident through such comparisons that the polarizability of [P═N] is less than that of a conjugated [C═C] bond but significantly more than a nonconjugated [C═C] bond. This agrees with the capability of these polymers to be high refractive index materials and also appears to agree with the allylic nature of the associated [P═N] bonding.[35] The lone pair electrons on the nitrogen atom in the phosphazene bond may be responsible for this observed polarizability. However, it appears that this alone is not enough to account for the molar refractivity values obtained. Because R_m is much larger for [P═N] than for either [C≡N] or [3°(N)], most of the polarizability of this structure may arise from either the phosphorus atom electrons or the electrons that comprise the P═N bond. It would be interesting to compare R_m[P═N] with other inorganic polymers such as polysiloxanes or polysilanes. However, no data were found for these systems. The polysulfur repeat unit structure [S−S] had an R_m that was slightly higher than R_m[P═N]. This is in agreement with the larger electron density associated with the S−S bond.

Conclusions

The molar refractivity contribution of the [P═N] repeat unit structure has been estimated to have a value of R_m[P═N] = 14.36 cm^3/mol. This is close to the R_m value of a conjugated [C═C] bond.[32] The optical dispersion for polyphosphazene type polymers was determined through measurement of the wavelength-dependent refractive index for two selected polyphosphazenes. The optical dispersion associated with these systems was found to be comparable to the values seen for conjugated, carbon-based, high refractive index polymers.[32] However, polyphosphazenes have several advantages over the organic-backbone polymers. They are usually amorphous, colorless materials with a backbone that is especially stable to photo or photooxidative breakdown.[34,41] Thus, polyphosphazenes may be good alternatives to conjugated, aromatic polymers in high refractive index applications.

Experimental Section

Materials. Polymers **1**−**9** were synthesized by reaction of the corresponding sodium salt of the side-group moieties with poly(dichlorophosphazene). This was accomplished in either dry THF or dry dioxane solvent under inert atmosphere conditions. The details of the syntheses and characterization of these polymers are described elsewhere.[40]

Preparation of Thin Films. Thin films of polymers **7** and **8** were prepared on both fused silicon substrates and quartz disks by spin coating a concentrated solution (5−7 wt %) of the polymer dissolved in either chlorobenzene or DMF.[44] The resulting films were dried thoroughly before ellipsometric and transmission measurements.

Density Measurements on Polymers. The densities of polymers **1**−**9** were measured using pychnometric methods.[45] Measurements were taken of the volume of a fluid displaced by a known mass of polymer sample, at 25 °C. From this, the densities of the polymers were calculated. Distilled, deionized water was used as the liquid because of the complete insolubility of these polymers in this medium.

Optical Measurements. Ellipsometric data were acquired using a J. A. Woollam Co. variable-angle spectroscopic ellipsometer (VASE, horizontal stage) equipped with a CVI Digikrom 242 double-grating monochromator. δ and ψ were measured from 300 to 1700 nm using 3 angles of incidence (i.e., for silicon, 670, 710, and 750; 10.0050) as sample replicates. A dynamic signal averaging routine was used which attempts to compensate for the nonlinearity of the xenon lamp light source over this wavelength region. Transmission data were also acquired with the Woollam instrument from 230 to 1700 nm. The 1340−1460 nm region was not used as this contained absorption features associated with the instrument fiber optic.

Molar Refractivity Calculations. All molar refractivity calculations were carried out in a similar manner. The following calculation for polymer **1** is typical. The experimental value of R_m for [NP(OPh)$_2$] was obtained with the Lorentz−Lorenz equation, using values of $n_{550} = 1.620$ and $\rho = 1.18$ g/mL. This gave a value of $R_m = 68.77$ cm^3/mol. An estimate of R_m was then obtained for [NP(OPh)$_2$] using the following formula:

$$R_m[\mathrm{NP(OPh)_2}] = R_m[\mathrm{N{=}P}] + 2\{R_m[\mathrm{C_6H_6}] - R_m[\mathrm{H_{arom.}}] + R_m[\mathrm{O_{arom.}}]\}$$

Here, $R_m[C_6H_6]$ was calculated with the Lorentz−Lorenz equation, using the literature values for benzene of $n_D = 1.5011$ and $\rho = 0.8765$ g/mL.[46] This gave a value of $R_m[C_6H_6] = 26.26$ cm^3/mol. Values of $R_m[H_{arom.}] = 0.59$ cm^3/mol and $R_m[O_{arom.}] = 1.77$ cm^3/mol were obtained from reference tables of the Lorentz−Lorenz molar group contributions ($\lambda = 589$ nm).[31] Substitution of the appropriate values into the above expression gave

$$68.77\ \mathrm{cm^3/mol} = R_m[\mathrm{N{=}P}] + 54.88\ \mathrm{cm^3/mol}$$

or

$$R_m[\mathrm{N{=}P}] = 13.89\ \mathrm{cm^3/mol}$$

Calculations were carried out for the remaining polymers (**2**−**9**) using analogous methods, with the following values:

$$R_m[\mathrm{C_6H_5Br}] = 33.95\ \mathrm{cm^3/mol}$$

$$R_m[\mathrm{C_6H_5I}] = 39.14\ \mathrm{cm^3/mol}$$

$$R_m[\mathrm{OCH_2CH_2O}] = 12.66\ \mathrm{cm^3/mol}$$

$$R_m[\mathrm{C_{10}H_8}] = 42.18\ \mathrm{cm^3/mol}$$

$$R_m[\mathrm{2\text{-}Br\text{-}C_{10}H_7}] = 46.38\ \mathrm{cm^3/mol}$$

$$R_m[\mathrm{2\text{-}I\text{-}C_{10}H_7}] = 57.90\ \mathrm{cm^3/mol}$$

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(44) For polymer **7** the films were 2900 Å thickness on quartz for the ellipsometry spectrum, 3084 Å on quartz for the transmission spectrum, and 3205 Å on silicon for an ellipsometry spectrum. For **8** the values were 1870 Å on silicon for ellipsometry and 1453 Å on quartz for the transmission spectrum.
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