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The functional group contribution to molar refraction and refractive index of pi-conjugated polymers has been evaluated from the available refractive index dispersion data for 33 conjugated polymers. The Lorentz-Lorenz molar refraction (R_{LL}) of 24 functional groups commonly found in conjugated polymers was determined and tabulated at selected wavelengths between 700 and 2500 nm to provide a basis for the computational prediction of the refractive index of conjugated polymers. A significant improvement on the accuracy of semiempirical prediction of the refractive index of conjugated polymers was achieved by using the new R_{LL} data (0.9% average error) compared to previous literature molar refraction data (14.8% average error). The new molar refraction data accounted well for the effects of optical dispersion, pi-electron delocalization, and molecular structure on the refractive index of conjugated polymers. The wavelength dependent refractive indices of several well-known conjugated polymers, trans-polyacetylene, poly(p-phenylene), poly(p-phenylenevinylene), poly(2,5-dimethoxy-p-phenylenevinylene), polythiophene, and poly(2,5-thiophenediylvinylene), were predicted from the new molar refraction data.

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Group Contribution to Molar Refraction and Refractive Index of Conjugated Polymers

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Abstract

The functional group contribution to molar refraction and refractive index of π-conjugated polymers has been evaluated from the available refractive index dispersion data for 33 conjugated polymers. The Lorentz-Lorenz molar refraction (R_{LL}) of 24 functional groups commonly found in conjugated polymers was determined and tabulated at selected wavelengths between 700 and 2500 nm to provide a basis for the computational prediction of the refractive index of conjugated polymers. A significant improvement on the accuracy of semi-empirical prediction of the refractive index of conjugated polymers was achieved by using the new R_{LL} data (0.9% average error) compared to previous literature molar refraction data (14.8% average error). The new molar refraction data accounted well for the effects of optical dispersion, π-electron delocalization, and molecular structure on the refractive index of conjugated polymers. The wavelength dependent refractive indices of several well-known conjugated polymers, *trans*-polyacetylene, poly(*p*-phenylene), poly(*p*-phenylene vinylene), poly(2,5-dimethoxy-*p*-phenylene vinylene), polythiophene, and poly(2,5-thiophenediyl vinylene), were predicted from the new molar refraction data.

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Introduction

The optical and nonlinear optical properties of polymers[1-14], particularly π-conjugated polymers, are of growing interest in view of their expected applications in photonics. integrated optics, optical communication, and optoelectronics. A review of the literature shows that whereas much theoretical and experimental work on the *nonlinear* optical properties of conjugated polymers has been reported in hundreds of research papers, many review papers[3], numerous edited volumes[1], and some monographs[2], there are very few reports on studies of the *linear* optical response such as the refractive index of the materials.[11-14] This should be suprising since it implies that we currently know more about the nonlinear optical properties of conjugated polymers than their linear optical properties. Yet, one should think that understanding of the nonlinear optical properties presupposes and requires prior knowledge and understanding of the linear optical response of the materials. Furthermore, information on the linear optical properties of conjugated polymers is also of interest to those studying the physical, chemical, and molecular properties of these polymers by optical techniques, e.g. light scattering for the determination of molecular weight, size, and shape.[15-17] Our study reported here, therefore, focuses on the semi-empirical correlation of structure with the refractive index of π-conjugated polymers.

There is a large body of experimental data on the refractive index at 589 nm (n_D) for many classes of organic, *nonconjugated* polymers.[15-17] Also, a number of semi-empirical group-contribution methods derived from the refractive indices of liquid organic compounds as well as organic polymers have been well-established to give reliable predictions of the refractive indices of nonconjugated polymers.[15,16] These group-contribution calculations are based on the *molar refraction* as the additive function and different models of the refractive index such as those due to Lorentz-Lorenz[18], Gladstone-Dale[19], Vogel[20], and Looyenga[21], respectively. The molar refraction values corresponding to these group-contribution models

have been collected extensively in van Krevelen's book and have been found to predict the refractive index of nonconjugated polymers in very good agreement with experimental data, showing deviations within 1%.[15] More recently, Bicerano[22] has developed a different approach based on the connectivity indices of molecules and obtained an accurate prediction of the refractive indices of organic (nonconjugated) polymers. The fundamental assumption of the semi-empirical group-contribution formalisms is the *additivity* of properties of functional groups such as molar refraction.[15,16] However, as it is well-known, any significant cooperative effects among functional groups can invalidate the additivity principle.[15,16] This implies that existing molar refraction values which completely neglect the cooperative phenomenon of *π-electron delocalization* cannot be accurate for predicting the refractive indices of conjugated polymers. This indeed is what has been found experimentally.[11-14] For example, our laboratory has found that the Lorentz-Lorenz model prediction based on existing molar refraction values at 589 nm underestimates the refractive index of conjugated polymers by as much as 22%.[12] The other models were equally as bad or worse in predictions. The reasons for the large deviations from experimental data, we believe, are that the large optical dispersion and the π-electron delocalization effects on the refractive index of conjugated polymers are not taken into account in the currently available molar refraction values of functional groups.

In this paper, we report the use of a semi-empirical group-contribution approach to determine new Lorentz-Lorenz molar refraction (R_{LL}) values for functional groups commonly found in p-conjugated polymers. The choice of the Lorentz-Lorenz model and hence R_{LL}, rather than other models, is owing to its theoretically sound basis for understanding the optical properties of dielectric materials.15,18 The conjugated polymers that form the refractive index data base for the present study are diverse in their structures so that structural effects on the refractive index such as polymer backbone variation and side-group substitution can be

captured in the set of functional groups extracted and the resulting molar refraction values. The p-conjugated polymers from which the set of 24 functional groups were obtained are shown in Chart I, representing four main classes of polymers : aromatic polyimines11,23, polyquinolines12,24, polyanthrazolines12,24, and polybenzobisazoles14,25. We have previously reported the third-order nonlinear optical properties of these p-conjugated polymers.4 Although the size of the data base (33 polymers) used in this study to formulate a group contribution to the refractive index of conjugated polymers is relatively small compared to similar correlations for nonconjugated polymers, a particular advantage of the new molar refraction values is that wavelength dispersion and p-electron delocalization are taken into account in predicting the usually significantly dispersed refractive indices of conjugated polymers in the visible and near-IR spectral range. The main limitation on the size of the data base was the lack of available wavelength dependent refractive index, $n(\lambda)$, of conjugated polymers other than those which have been studied extensively in our laboratory.[11-14] Another important limitation of the present results is that the $n(\lambda)$ data are for the average *in-plane* refractive index (n_{TE}) since the birefringence ($\Delta n = n_{TE} - n_{TM}$) was not measured. Nevertheless, it will be shown that the new R_{LL} data can be used to correlate and predict fairly accurately the refractive indices of conjugated polymers.

Experimental and Computational Section

Preparation of Thin Films of Polymers. The synthesis and characterization of the four series of polymers have been described in detail in our previous studies.[10b,23-25] Optical-quality thin films (~1–4 μm) of the polymers were prepared by spin coating of concentrated solutions of the Lewis acid (e.g., $GaCl_3$ and $AlCl_3$) or diarylphosphate complexes of the polymers in nitromethane or m-cresol, respectively. Details of the preparation of the soluble complexes and the preparation of thin films of the pure polymers were described

previously.[23-25] Of particular interest is the ability to significantly reduce the crystallinity of the polymer thin films through this complexation-mediated solubilization and processing compared to the semicrystalline pristine polymers.[23,26,27] It has been shown that amorphous thin films of the polymers can be obtained by regulating the amount of complexation reagent used in the preparation of soluble complexes.[26,27]

Refractive Index Dispersion Data. The refractive index was deduced from the interference fringes in the transmission spectrum, which was taken on a Perkin-Elmer Lambda 9 UV-vis-near IR spectrophotometer at room temperature with the probe beam perpendicular to the plane of the film.[11,28] The wavelengths where the transmission maximum and minimum occurred were recorded and used as input to a computation program to calculate the refractive indices.[11] The film thickness was independently measured to be in the range of 1.0–4.0 μm for all films by using an Alpha step profilometer. The variation of film thickness in a scan of 2000 μm linear distance, was less than 1%.[11] To confirm that the measured refractive index is isotropic in the plane of the film and therefore represents a property corresponding to the molecular structure, different films of the same polymer prepared at different times from different solutions were measured to reproduce the same refractive index data. The effects of crystallinity and orientation on refractive index were proven negligible by the reproducibility of the refractive index data of the same polymer.[11] Since the probe beam is perpendicular to the plane of the film in this experiment, the electric vector of light is parallel with the plane of the film, hence the measured refractive index is the *isotropic average in-plane* value (n_{TE}). The birefringence ($\Delta n=n_{TE}-n_{TM}$) was not measured in the present study.

To provide a concise summary of the refractive index dispersion data, a three-term Sellmeier equation was used to fit the data.[11] It has been shown in many studies that the Sellmeier equation gives a good description of the refractive indices of not only inorganic glasses and non-glass materials but also of organic molecules and polymers.[29-31] In our previous study, the applicability of this equation to the refractive indices of conjugated

polymers was demonstrated.[11] This equation is written as :[32]

$$n^2 = 1 + \sum_{s=1}^{3} \frac{a_s \lambda^2}{\lambda^2 - b_s^2} \qquad (1)$$

where n is the refractive index, λ is the wavelength in micrometers (μm), a_s is a constant related to the oscillator strength, and b_s is the resonance wavelength (in μm) of refractive index. All the refractive index dispersion data of the 33 polymers in Chart I were reported as the three-term Sellmeier equation as listed in Table 1. These data were used in the computation of the molar refraction of various functional groups in conjugated polymers.

Functional Group Contribution to Molar Refraction Based on Lorentz-Lorenz Model. The celebrated Lorentz-Lorenz theoretical model provides a simple and accurate correlation between refractive index, polarizability, and molar volume.[15,18] This model shows that the refractive index n, a bulk material property, increases with increasing molecular polarizability α, but decreases with increasing molar volume V. This equation is written as :

$$\left(\frac{n^2-1}{n^2+2}\right) V = \frac{4\pi}{3} N_A \alpha \qquad (2)$$

in which N_A is the Avogadro's number. In terms of group contribution to refractive index, the molecular polarizability is expressed as the sum of the polarizabilities of the constituent functional groups.[15-17] Alternatively and equivalently, the polarizability is usually expressed as the sum of the molar refraction of functional groups of the organic molecules and polymers :[15-17]

$$\left(\frac{n^2-1}{n^2+2}\right) V = \sum_i (R_{LL})_i \qquad (3)$$

in which $(R_{LL})_i$ is molar refraction (cm^3/mol) of a functional group i. For a polymer, V and

$(R_{LL})_i$ are the molar values corresponding to the polymer repeat unit.

Representative functional groups that are the constituent components of the conjugated polymers in Chart I were selected for the computation of molar refraction. These functional groups were selected according to two criteria. First, the functional group should be sufficiently large so that the effects of π-electron delocalization on refractive index of conjugated polymers can be properly accounted for. Secondly, the selected functional groups should be representative among various conjugated polymers so that the resulting R_{LL} values can be easily used to predict the refractive indices of a large number of conjugated polymers. Consequently, a set of 17 basic functional groups was initially selected and the correponding molar refraction values were determined by computation. Next, an additional set of 7 functional groups (groups 2, 3, 7, 8, 12, 13 and 15 in Table 2) consisting of larger units was chosen and the molar refraction was determined by computation. The structures of the resulting set of 24 functional groups are shown in Table 2. The 7 larger functional groups are actually a combination of some of the basic functional groups and therefore a comparison of their molar refraction with that of the more basic functional groups should provide information about the effects of electron delocalization on molar refraction.

The molar volume of each polymer repeat unit was calculated separately by using the tabulated group-contribution molar volumes of functional groups in glassy polymers.[15] The measured refractive index data in the form of the three-term Sellmeier equation and the molar volumes of the polymer repeat units were then used as input to a computation program. The Lorentz-Lorenz molar refraction R_{LL} was calculated by the least-squares fit of Equation (3) to the data. This was done by solving a set of 24 linear equations with Gaussian elimination.[33]

Results and Discussion

On the basis of our refractive index dispersion data of the 33 conjugated polymers in the 700–2500-nm wavelength range,[11-14] the Lorentz-Lorenz molar refraction R_{LL} was determined

for each of the 24 selected functional groups. The new R_{LL} data base provides a basis for the prediction of the refractive index of conjugated polymers by using the group-contribution approach which assumes additivity of R_{LL} values. We note that the additivity principle is valid here because the effects of π-electron delocalization have already been accounted for in the new R_{LL} values of Table 2. The molar refraction data for the 24 functional groups include the effects of optical dispersion on refractive index and hence can be used to predict the modified Abbe number $\nu_d'=(n_{1319nm}-1)/(n_{1064nm}-n_{2500nm})$ which is a numerical measure of the optical dispersion of the refractive index of conjugated polymers in the near infrared.[11] The molar refraction of functional groups is of interest *per se* since it is a fundamental molecular property which is directly related to the molecular polarizability.[15-18,34] The polarizability of the functional groups are obtained readily by : $\alpha=3R_{LL}/4\pi N_A$. In the following, we present the molar refraction values at selected wavelengths as well as $R_{LL}(\lambda)$ spectra in the 700–2500 nm range to elucidate the effects of molecular structure and π-electron delocalization on molar refraction and to illustrate the use of the R_{LL} data to predict the refractive index of conjugated polymers.

Molar Refraction of Functional Groups in Conjugated Polymers. Table 2 lists the molar refraction of the functional groups investigated in the present study. The molar refraction data are tabulated at four wavelengths : 700, 1064, 1319, and 2500 nm. The 700-nm data correspond to the shortest wavelength used in the measurement of transmission spectra and hence $n(\lambda)$, whereas the 2500-nm data can be regarded as nonresonant values of the refractive indices.[11] The data at 1064 and 1319 nm are provided in view of the commercial laser lines at these wavelengths and therefore they are of practical interest for potential optical and optoelectronic applications of conjugated polymers.[35] It has been suggested in our previous study that a modified Abbe number defined by the refractive indices at 1064, 1319, and 2500 nm is an adequate numerical measure of the optical dispersion of the refractive indices of conjugated polymers.[11] Also listed in Table 2 are the molar volumes of the 24

functional groups which were calculated from the group-contribution to molar volume of polymers in the literature.[15]

The molar refraction values in Table 2 are molecular quantities derived from bulk refractive indices. The underlying assumption is that effects of morphology, such as the preferential orientation of polymer chains and crystallinity, are negligible. Considerable care was taken to ensure that the films used to measure the refractive index were isotropic and amorphous as previously described;[11-14] reproducibility of $n(\lambda)$ data for a given polymer by using films with different thicknesses was demonstrated. However, the R_{LL} data from amorphous solid conjugated polymers should allow structure-refractive index correlations of amorphous as well as semicrystalline conjugated polymers. The reason is that with development of significant crystallinity V decreases while R_{LL} increases and so resulting in no significant net change of refractive index. Perhaps the most important limitation of the present $n(\lambda)$ data from which R_{LL} values were generated is that they are the average *in-plane* values (n_{TE}). The corresponding *out-of-plane* refractive index values (n_{TM}) through which the extend of birefringence ($\Delta n = n_{TE} - n_{TM}$) could be assessed was not measured.

Table 2 shows that the molar refraction varies significantly with structure and wavelength. The nonresonant molar refraction at 2500 nm is in the range of 15.66 for *trans*-vinylene functional group to 89.07 cm^3/mol for 2,2'-bithiophene-5,5'-diyl functional group. Approaching the short-wavelength region, the molar refraction is increased as a result of one-photon resonance enhancement near the π-π^* absorption band of the conjugated polymers. The resonance-enhanced molar refraction at 700 nm is increased considerably relative to the 2500-nm value. For example, the 700-nm molar refraction is about a factor of 1.3 larger than that at 2500 nm for the *p*-phenylene functional group (Table 2). The effect of optical dispersion on refractive index is, therefore, very important for the linear optical properties of conjugated polymers in the visible and near-IR wavelength range.

Accuracy of Prediction of Refractive Index. With the tabulated molar refraction

data, the refractive indices of conjugated polymers can be predicted using the group-contribution formulation based on the Lorentz-Lorenz model. To illustrate the improvement on the accuracy of prediction of the refractive index of conjugated polymers, calculations were performed by using Equation (3). The measured refractive indices of the 33 conjugated polymers at 2500 nm as well as their refractive indices at 589 nm (extrapolated by the Sellmeier equation parameters in Table 1) are given in Table 3. Also shown in Table 3 for comparison are the predicted refractive indices $(n_{LL})_{old}$ obtained by using the previous literature molar refraction data at 589 nm (sodium D line). One notes a large deviation between the 589-nm data (i.e. $nl_{589\ nm}$) and the predicted $(n_{LL})_{old}$ with an average error of 14.8%. A comparison of $(n_{LL})_{old}$ with the 2500-nm data ($nl_{2500\ nm}$) of the conjugated polymers still shows an average error of 4.6% which is far from an acceptable error in refractive index. In contrast, significant improvements on the predicted refractive indices are obtained by using the new R_{LL} values as seen by comparing $(n_{LL})_{new}$ to the 2500-nm data in Table 3. A dramatically smaller average prediction error of 0.9% is obtained. The improved accuracy of prediction of the refractive index of conjugated polymers by using the new R_{LL} values is obviously because the effects of π-electron delocalization and optical dispersion are automatically included in the new molar refraction values. Further improvement of the accuracy of prediction should result from an increase of the $n(\lambda)$ data base from the present 33 conjugated polymers.

Effects of π-Electron Delocalization and Molecular Structure on R_{LL}. Figure 1 shows the wavelength dependent molar refraction $R_{LL}(\lambda)$ of three related functional groups : *p*-phenylene, *p*-biphenylene, and *p*-terphenylene. All three molar refraction data in Figure 1 indicate that optical dispersion is significant. As a result of optical dispersion there is about a factor of 1.2 increase of the molar refraction of each functional group in Figure 1 in going from 2500 nm to 700 nm. The results of Figure 1 also reveal effects of π-electron delocalization on R_{LL}. The molar refraction of *p*-phenylene at 2500 nm is 28.98 cm^3/mol whereas a progressive increase to 64.34 and 90.74 cm^3/mol (Table 2) for *p*-biphenylene and

p-terphenylene, respectively, is observed at the same wavelength.

Similar plots of the molar refraction dispersion of 2,5-thiophenediyl and 2,2'-bithiophene-5,5'-diyl functional groups and of *trans*-vinylene and *trans,trans*-divinylene functional groups are shown in Figures 2 and 3, respectively. A significant larger molar refraction is observed in the thiophene series (Figure 2) relative to the *p*-phenylene series (Figure 1), indicating nonresonant R_{LL} values of 40.72 and 89.07 cm^3/mol for 2,5-thiophenediyl and 2,2'-bithiophene-5,5'-diyl, respectively (Table 2). From Table 2 and Figure 3, one sees that the molar refraction of *trans*-vinylene at 2500 nm is 15.66 cm^3/mol and that of *trans,trans*-divinylene is 33.33 cm^3/mol. At 2500 nm, the ratios of the molar refractions of bithiophene to thiophene and divinylene to *trans*-vinylene are 2.18 and 2.13, respectively.

Figure 4 shows the plot of $R_{LL}/(R_{LL})_0$ as a function of N for the *p*-phenylene, thiophene, and *trans*-vinylene series of functional groups at 2500 nm, where N is the number of the basic functional group (e.g. *p*-phenylene) units and $(R_{LL})_0$ corresponds to the molar refraction for the case N=1. A linear relationship holds approximately for the three series of functional groups, i.e. $R_{LL} \sim N$. In contrast, many theoretical and experimental studies[36] of the scaling of polarizability (α), hyperpolarizability (β), and second hyperpolarizability (γ) with the number of units (or monomers) N in oligomers or sequentially build chain molecules generally predict superlinear dependence on N. In the case of the polarizability (or molar refraction) of conjugated molecules and N-oligomers, the predicted scaling[36] is $\alpha \sim R_{LL} \sim N^m$ with m=2 to 3. The dashed line in Figure 4 is such a predicted[36] dependence of molar refraction on N, i.e. $R_{LL} \sim N^3$. There is clearly a dramatic difference between the scaling law obeyed by R_{LL} measured from the refractive indices of conjugated polymers and that obeyed by R_{LL} of sequentially built N-oligomers. This difference is not suprising as it originates in the different things being measured. In the case of sequentially built N-oligomers, the molar refraction of a monomer unit within the N-oligomer would vary with the size of the oligomer.

For example, the 2,5-thiophenediyl group in α-terthiophene and that in α-sexithiophene would have dramatically different R_{LL} values if deduced from the polarizability of these oligomers. By deducing molar refraction from the refractive indices of many conjugated polymers (large N limit) one is breaking up the different conjugated polymers into selected constituent functional groups and distributing the cooperative properties of the polymers among the constituent functional groups. This procedure is essentially a linearization process. Thus, the molar refraction of the 2,5-thiophenediyl functional group, for example, should be fairly constant regardless of what specific conjugated polymer it is found in.

The observed linear relationship between molar refraction and the number of identical functional groups (i.e. $R_{LL} \sim N$) (Figure 4) suggests that the additivity principle for R_{LL} is valid even in π-conjugated polymers. This means that the group contribution approach can be used to predict the refractive indices of π-conjugated polymers by using the new R_{LL} values and functional groups (Table 2).

The effects of π-electron delocalization on molar refraction can be further illustrated by comparing the present molar refraction of functional groups to the reported polarizability values of conjugated small molecules.[34] The polarizability, calculated by $\alpha = 3R_{LL}/4\pi N_A$, is 1.6×10^{-23} and 3.5×10^{-23} cm^3 for the 2,5-thiophenediyl and 2,2'-bithiophene functional groups, respectively. These values are significantly larger than the reported 9.8×10^{-24} cm^3 and 2.5×10^{-23} cm^3 for the thiophene and 2,2'-bithiophene molecules,[34] respectively. This comparison indicates that the remarkably enhanced polarizability due to π-electron delocalization can be properly accounted for in the group contribution method of deducing molar refraction from the refractive indices of π-conjugated polymers.

A comparison of the molar refractions of the large functional groups and the smaller (basic) functional groups was also made on various combinations. It was found that the large functional groups have slightly larger (~10–15 %) molar refraction than the sum of the corresponding smaller functional groups. For example, the molar refraction of group 8 in

Table 2 is 84.83 cm^3/mol at 2500 nm, which is to be compared with 73.62 cm^3/mol by adding the molar refraction of group 1 and 11 (2x28.98+15.66=73.62). However, an exception is noted in group 7 that has a molar refraction of 60.86 cm^3/mol at 2500 nm, a value that is smaller than 78.32 cm^3/mol obtained by adding the molar refraction of group 1, 6 and 11 (28.98+33.68+15.66 =78.32). This may be a result of interruption of conjugation between the two dissimilar groups, *p*-phenylenevinylene and *p*-phenyleneimine, which thereby decreases polarizability. It is interesting to note that a reduced second hyperpolarizability (γ) has also been observed in the conjugated polyimine (polymer 11 in Chart I) consisting of these two dissimilar functional groups.[37] The implication of this is that in choosing functional groups to simulate the repeat unit of a polymer whose refractive index is to be predicted the largest possible functional group should be used. Also, the number of functional groups combined to achieve the desired polymer should be minimized.

Another interesting observation on the effects of electron delocalization on R_{LL} is illustrated by comparing the molar refraction of functional groups with electron-donating side group substitution. As a result of the electron-donating ability of side groups, electron delocalization is expected to be more efficient in functional groups with side group substitutions compared to functional groups without substitutions or with weaker electron-donating side groups. Figure 5 shows the wavelength dispersion of the molar refraction of 2-methyl-*p*-phenylene, 2-methoxy-*p*-phenylene, and 2,5-dimethoxy-*p*-phenylene functional groups along with that of the *p*-phenylene functional group for comparison. In the whole spectral range, the molar refraction of 2-methyl-1,4-phenylene is almost equal to the molar refraction of *p*-phenylene. The closeness of the molar refractions of *p*-phenylene and 2-methyl-1,4-phenylene can be attributed to the compensation of the effects of weak electron donating and steric hindrance due to methyl substitution. Interestingly, the corresponding polymers, PPI and PMPI (polymers 1 and 2 in Chart I), also have identical λ_{max} and absorption edge in their optical absorption spectra.[23a] Another electron-donating side group,

methoxy substitution, results in a noticeable enhancement of molar refraction as evidenced by comparing the molar refraction dispersion of 2-methoxy-1,4-phenylene and 2,5-dimethoxy-1,4-phenylene functional groups with that of the *p*-phenylene functional group in Figure 5. At 2500 nm, the molar refraction are 36.45 and 43.77 cm^3/mol for 2-methoxy-1,4-phenylene and 2,5-dimethoxy-1,4-phenylene, respectively (groups 22 and 23 in Table 2). Both functional groups have significantly increased molar refraction relative to the 28.98 cm^3/mol for *p*-phenylene. A similar enhancement of molar refraction by electron-donating side group is also observed in the dihydroxy-substituted *p*-phenylene functional group (group 24 in Table 2).

Finally, a direct indication of the effects of π-electron delocalization on molar refraction is a comparison between our R_{LL} data obtained from the refractive indices of π-conjugated polymers and the previous R_{LL} data at 589 nm. Only a few functional groups collected in Table 2 can be found in previous work by van Krevelen who reported groups 1, 2, 11, and 21 to have R_{LL} values of 25.03, 50.06, 8.88, and 29.9 cm^3/mol, respectively, at 589 nm. Our R_{LL} values for these four functional groups (1, 2, 11, and 21 in Table 2) at 700 nm are respectively 36.96, 74.42, 16.95, and 36.27 cm^3/mol which are larger than previous values at 589 nm by factors of 1.2 to 1.9. The significantly larger R_{LL} values reported here compared to the literature values mean that these functional groups are more polarizable when incorporated into π-conjugated polymers than when incorporated into small molecules or nonconjugated polymers. Thus, as expected, a *trans*-vinylene group, for example, in a conjugated polymer such as polymer 27 or 28 (Chart I), *trans*-polyacetylene, or poly(*p*-phenylenevinylene) is dramatically more polarizable, and hence has a larger molar refraction, than the same group incorported in *trans*-butadiene or *trans*-polybutadiene. Similar conclusions can be drawn about the polarizability and molar refraction of all the functional groups collected in Table 2.

Effects of Heteroatoms. From the refractive index data base for conjugated polymers, the effects of heteroatoms on molar refraction can be readily elucidated because all

the polymers in Chart I contain heteroatoms in their structures. The diverse polymer structures also provide an opportunity to compare the effects of different heteroatoms (S, O, N) on molar refraction. As already shown in Figures 1 and 2, the larger molar refraction of heterocyclic rings compared to aromatic rings is readily seen by comparing the molar refraction of 2,5-thiophenediyl and *p*-phenylene functional groups. This difference is mainly due to the highly polarizable sulfur atom as compared to the carbon atom. It is of interest to compare the relative order of sulfur, oxygen, and nitrogen atoms in changing the molar refraction. Figure 6 shows the molar refraction dispersion of benzobisthiazole (a), benzobisoxazole (b), and benzobisimidazole (c) functional groups (groups 15, 16 and 17 in Table 2) which contain sulfur, oxygen, and nitrogen atoms, respectively. At 2500 nm, the molar refraction of benzobisthiazole, benzobisoxazole, and benzobisimidazole functional groups is 45.25, 38.20, and 30.45 cm^3/mol (Table 2), respectively. The order of molar refraction of these three members of the benzobisazoles is benzobisthiazole > benzobisoxazole > benzobisimidazole, and therefore the corresponding order of refractive power of the heteroatoms is S > O > N. However, it is worth noting that the effects of sulfur and oxygen atoms on third-order nonlinear optical properties have been shown to be comparable in a study of the third-order optical susceptibility of polybenzobisthiazole and polybenzobisoxazole.[4(a)]

Predictions of Refractive Indices of Other Conjugated Polymers. The functional groups and the molar refraction data in Table 2 provide a basis for the group-contribution calculation of the refractive index of any conjugated polymer whose repeat unit can be constructed from one or more of the 24 functional groups. To illustrate the applicability of the tabulated molar refraction data, predictions of the optical dispersion of the refractive indices of several well-known π-conjugated polymers, such as *trans*-polyacetylene (*trans*-PA) and poly(p-phenylenevinylene) (PPV), were made. This was done by choosing a proper combination of functional groups in Table 2 to represent the polymer repeat unit and thereby calculate the refractive index according to Equation (3). For example, the molar refraction of

the repeat unit of *trans*-polyacetylene was chosen as one half of the value of R_{LL} for the *trans,trans*-divinylene functional group (16.67 cm^3/mol at 2500 nm, group 12 in Table 2). From this R_{LL} value together with the corresponding molar volume (27 cm^3/mol, Table 2) the refractive index of *trans*-PA was determined to be 2.44 at 2500 nm. The molar refraction of the repeat unit of poly(*p*-phenylene) (PPP) was obtained from one third of that of the *p*-terphenylene functional group. The molar refraction of PPV repeat unit was obtained as a combination of that of the *p*-phenylene and *trans*-vinylene functional groups. Similar procedures for selecting functional groups were used for determining the repeat units of poly(2,5-dimethoxy-1,4-phenylene vinylene) (DMO-PPV), poly(2,5-thiophenediyl) (PT) and poly(2,5-thienylene vinylene) (PTV) in order to determine their repeat-unit molar refractions.

Figure 7 shows the predicted isotropic of refractive indices of *trans*-PA (a), PPV(b), PPP(c), and DMO-PPV(d). The predicted refractive indices of PT and PTV are shown in Figure 8. From Figure 7 and Table 4 one sees that trans-polyacetylene has a predicted isotropic refractive index of 2.66–2.43 in the 700–2500 nm spectral range. PPP has $n(\lambda)$ of 2.13–1.89 (Table 4) in the same spectral range. PPV has predicted isotropic refractive indices of 2.28–1.95, in the 700–2500 nm range, which are intermediate beween the $n(\lambda)$ values of *trans*-PA and PPP. Although PPV can be regarded as an alternating copolymer of *trans*-vinylene and *p*-phenylene, and hence compositionally and symmetrically intermediate beween *trans*-PA and PPP, it is to be noted that its refractive index is much closer to that of PPP than an average between the refractive indices of *trans*-PA and PPP. Introduction of electron-donating dimethoxy side groups in DMO-PPV results in significantly reduced refractive index (1.70–1.99) compared to PPV. Although the dimethoxy substitution significantly increases the efficiency of π-electron delocalization and hence a larger R_{LL} value (59.58 cm^3/mol at 700 nm) compared to *p*-phenylene (36.96 cm^3/mol at 700 nm), the corresponding increase in molar volume results in a net reduction of the refractive index of DMO-PPV. The predicted isotropic *in-plane* refractive indices (n_{TE}) of the thiophene-containing polymers, PT and PTV,

are shown in Figure 8. The n(λ) values for PT and PTV are quite high, being 3.90–2.77 and 3.56–2.42, respectively, in the 700–2500 nm range (Table 4). The refractive index of polythiophene is larger than that of *trans*-polyacetylene throughout the spectral range investigated. This is due in part to the contribution of the highly polarizable sulfur heteroatom.

An appropriate comparison between data and these group-contribution predicted refractive indices of conjugated polymers shown in Figures 7 and 8 and Table 4 could not be made because the necessary n(λ) data are not available. However, a sketchy comparison can be made. A film of *trans*-polyacetylene prepared by the Durham method was reported to exhibit a refractive index of 2.33 in the long-wavelength limit.[38] This value is very close to the predicted value of 2.44 at 2500 nm in Table 4. The refractive index of a stretched PPV film was reported as 1.59 in the perpendicular direction (n_{TM}) and 1.60 in the parallel direction (n_{TE}) of the film at 602 nm.[39] These reported values[39] give a birefringence ($\Delta n = n_{TE} - n_{TM}$) of only 0.01 which is rather small for a stretched film. However, the TE and TM waveguide modes of a PPV film have also been reported to give n_{TE} and n_{TM} refractive indices of 2.085 and 1.63, respectively at 632.8 nm.[40] The reported refractive index n_{TE} at 632.8 nm is in good agreement with the predicted 2.28–1.95 values in the 700–2500-nm wavelength range (Table 4). The large deviation of one of the repoeted data[39] with prediction may be an indication of incomplete conversion to the pure fully conjugated PPV from the nonconjugated precursor polymer whose refractive index is obviously much smaller than that of PPV.[39,40] The refractive indices of the other conjugated polymers in Table 4 (DMO-PPV, PPP, PT, and PTV) have not been reported at any wavelength, to our knowledge.

Conclusions

Our study reported here has for the first time addressed the problem of semi-empirical correlation of structure with the refractive index of conjugated polymers. We have determined the molar refraction of 24 functional groups by application of the group contribution

formalism and the Lorentz-Lorenz model to the currently available wavelength dependent refractive indices of 33 conjugated polymers. The present Lorentz-Lorenz molar refraction (R_{LL}) data for functional groups in conjugated polymers can be used to predict the isotropic *in-plane* refractive indices (n_{TE}) of π-conjugated polymers with average error of 0.9%, a significant improvement over the literature R_{LL} data (14.6% average error). The molar refraction of the functional groups in π-conjugated polymers was found to vary significantly with optical dispersion, π-conjugation length, heteroatoms, and molecular structure. As expected from the greater π-electron delocalization and the resulting higher polarizability, the functional groups in π-conjugated polymers have larger R_{LL} values compared to identical functional groups in small molecules or non-conjugated polymers. The new R_{LL} data were also used to predict the wavelength dependent refractive indices, n(λ), of several well-known π-conjugated polymers : *trans*-polyacetylene, poly(*p*-phenylene), poly(*p*-phenylene vinylene), poly(2,5-dimethoxy-1,4-phenylene vinylene), poly(2,5-thiophenediyl), and poly(2,5-thiophenediyl vinylene). The molar refraction data reported here also provide a direct quantitative information about the polarizability (α) of functional groups in conjugated polymers. Important limitations of the present results on the linear optical properties of conjugated polymers include the small n(λ) data base from which R_{LL} was established and the lack of information on birefringence.

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Table 1. Refractive-Index Dispersion Data Formulated in The Three-Term Sellmeier Equation[a]

polymer	a_1 b_1	a_2 b_2	a_3 b_3
1. PPI	0.0006±2.0E-5	2.1697±4.0E-4	0.0072±3.0E-5
	0.3059±4.0E-5	0.3061±2.0E-5	0.3056±1.0E-5
2. PMPI	0.0276±2.0E-4	0.0690±1.5E-3	1.6511±1.1E-3
	0.2586±2.0E-4	0.2581±8.0E-4	0.2625±1.0E-4
3. PMOPI	1.7129±9.0E-4	0.0004±7.0E-5	0.0039±4.0E-5
	0.3221±1.0E-4	0.3205±1.0E-4	0.3197±1.0E-4
4. PHOPI	2.0353±3.2E-3	0.0513±1.3E-3	0.0237±1.0E-4
	0.2902±2.0E-4	0.2932±2.0E-4	0.2929±8.0E-4
5. MO-PPI	1.8896±3.1E-3	0.0201±2.4E-3	0.0652±2.5E-3
	0.2967±3.0E-5	0.2986±1.0E-4	0.2989±1.0E-4
6. P3MOPI	0.0301±6.0E-4	1.5423±6.0E-4	0.0233±4.0E-4
	0.3908±1.0E-4	0.3883±1.0E-5	0.3907±1.0E-4
7. MO-PHOPI	0.8207±1.1E-2	0.6652±8.9E-3	0.5138±6.4E-3
	0.1251±3.6E-3	0.2473±1.0E-3	0.2735±1.9E-3
8. PPI/PMPI	0.7395±1.2E-3	0.5271±2.6E-3	0.6946±1.9E-3
	0.4033±4.0E-4	0.2464±2.0E-4	0.2705±1.6E-3
9. PBPI	2.0980±4.9E-3	0.0026±3.0E-4	0.0598±3.0E-3
	0.3549±1.0E-4	0.3558±1.0E-4	0.3561±4.0E-4
10. PTMOPI	0.0371±1.2E-4	1.9560±1.4E-4	0.0458+9.9E-5
	0.3577+4.6E-5	0.3495±7.4E-6	0.3579±4.9E-5
11. PSPI	0.6529±5.2E-3	0.7698±4.5E-3	0.4207±2.3E-3
	0.2354±8.0E-4	0.1723±2.0E-3	0.3795±9.0E-4
12. PSMOPI	1.4778±2.4E-3	0.0444±1.9E-3	0.1077±1.9E-3
	0.4351±2.0E-4	0.4495±2.0E-4	0.4512±7.0E-4
13. PBEPI	2.0049±4.0E-4	0.0152±1.0E-4	0.0464±3.0E-4
	0.2553±2.0E-5	0.2572±1.0E-4	0.2576±1.0E-4
14. 1,5-PNI	0.4195±1.4E-3	0.0381±1.1E-3	1.7027±1.3E-3
	0.4091±1.0E-4	0.4084±2.0E-4	0.3993±1.0E-4
15. 1,5-PMONI	0.7110±1.3E-3	1.0084±1.2E-3	0.3280±7.0E-4
	0.2969±1.0E-4	0.2589±2.0E-4	0.3359±2.0E-4
16. PPPQ	1.6344±6.4E-4	0.0767±4.3E-5	0.0597±6.4E-4
	0.2221±1.4E-5	0.2220±1.3E-4	0.2216±3.0E-6
17. PBPQ	0.0274±2.9E-5	0.0257±3.0E-4	2.0978±2.5E-4
	0.2809±1.3E-6	0.2810±1.3E-5	0.2817±1.0E-6
18. PSPQ	2.1600±1.7E-4	0.0001±1.5E-5	0.0211±1.7E-4
	0.2932±1.7E-7	0.2933±2.3E-6	0.2931±6.6E-6
19. PBAPQ	2.4656±3.0E-4	0.0172±2.8E-4	0.0159±2.3E-4
	0.2754±1.1E-5	0.2703±1.3E-5	0.2704±1.3E-4
20. PTPQ	1.8934±7.1E-4	0.0506±7.6E-4	0.1656±5.9E-4
	0.3605±9.8E-5	0.3421±2.1E-4	0.3399±5.1E-4
21. PBTPQ	0.0285±3.5E-4	0.0052±3.6E-4	2.5408±3.0E-4
	0.3456±6.1E-6	0.3457±2.7E-5	0.3463±1.2E-6
22. PPDA	0.0133±3.8E-4	1.8392±4.7E-4	0.0390±3.5E-4
	0.2924±1.1E-4	0.2886±1.4E-5	0.2930±8.4E-5

Table 1. continued

23. PBDA	0.7398±8.6E-3	0.6917±1.0E-2	0.7495±7.5E-3
	0.3237±6.8E-4	0.2211±1.1E-3	0.2541±4.7E-4
24. PSDA	0.0669±2.4E-4	0.0001±5.0E-5	2.1928±2.4E-4
	0.3094±2.1E-5	0.3100±1.5E-4	0.3122±1.9E-6
25. PBADA	1.9753±4.2E-4	0.0152±3.9E-4	0.0261±3.3E-4
	0.3205±4.9E-6	0.3190±1.4E-5	0.3189±5.5E-5
26. PBZT	0.8961±2.6E-3	0.1668±1.7E-3	0.7777±2.3E-3
	0.3196±3.5E-4	0.3647±3.9E-4	0.3345±2.1E-4
27. PBTV	1.9470±1.1E-4	0.0427±1.1E-4	0.0787±8.8E-5
	0.3810±8.4E-7	0.3800±1.7E-6	0.3799±1.2E-5
28. PBTDV	2.3929±6.0E-4	0.0161±4.7E-4	0.0188±4.2E-4
	0.3692±1.1E-5	0.3661±1.6E-5	0.3660±1.2E-4
29. PBTPV	0.0731±1.4E-3	2.6514±1.4E-3	0.0226±1.0E-3
	0.3776±9.7E-4	0.3809±1.7E-5	0.3781±1.9E-4
30. 14PNBT	0.0955±6.4E-5	0.0202±7.0E-5	1.9015±4.7E-5
	0.2997±3.2E-6	0.3002±1.5E-5	0.3023±3.7E-7
31. PBIDV	0.0710±9.4E-5	0.0020±9.5E-5	2.3644±7.7E-5
	0.3545±1.5E-6	0.3547±1.5E-5	0.3552±5.9E-7
32. PBIPV	1.7922±2.2E-3	0.0600±2.2E-3	0.0997±1.8E-3
	0.3535±4.2E-5	0.3498±5.3E-5	0.3495±2.6E-4
33. PBO	0.0599±6.0E-5	0.0132±6.3E-5	1.7854±4.8E-5
	0.3783±2.4E-6	0.3785±1.1E-5	0.3797±8.0E-7

[a] b_1, b_2, b_3 are in μm.

Table 2. Molar volume (V) and molar refraction (R_{LL}) of functional groups in conjugated polymers at selective wavelengths.

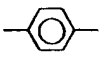
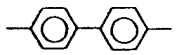
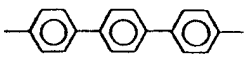
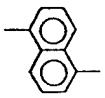
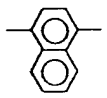
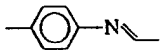
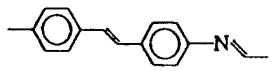
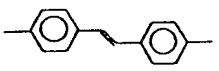
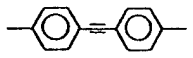
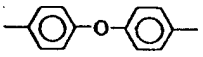
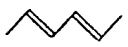
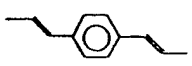
		R_{LL} (cm^3/mol)			
group	V (cm^3/mol)	700 nm	1064 nm	1319 nm	2500 nm
1. 	65.5	36.96	31.66	30.46	28.98
2. 	131.0	74.42	68.79	67.53	66.34
3. 	196.5	106.44	96.23	93.81	90.74
4. 	119.0	68.17	60.10	58.28	56.01
5. 	119.0	56.41	55.98	55.89	56.38
6. 	80.95	37.49	35.06	34.46	33.68
7. 	165.35	74.45	66.72	64.92	60.86
8. 	149.9	93.60	87.46	86.04	84.83
9. 	149.2	92.64	87.12	84.81	84.84
10. 	141.0	67.10	61.78	60.57	59.06
11. 	27.0	16.95	15.87	15.65	15.66
12. 	54.0	36.12	33.96	33.52	33.33
13. 	119.5	78.02	72.45	71.22	70.29

Table 2. continued

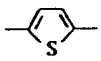
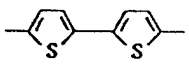
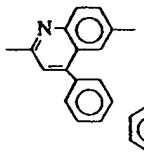
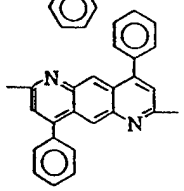
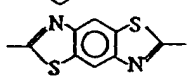
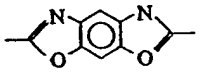
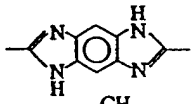
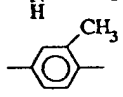
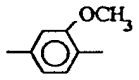
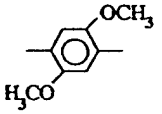
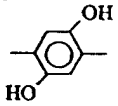
	group	V (cm^3/mol)	R_{LL} (cm^3/mol) 700 nm	1064 nm	1319 nm	2500 nm
14.		64.4	55.73	45.25	42.96	40.72
15.		128.8	106.45	94.59	91.88	89.07
16.		155.5	63.75	60.42	59.54	58.10
17.		249.2	99.57	92.12	90.23	87.18
18.		130.0	57.25	49.96	48.16	45.25
19.		110.0	53.03	43.76	41.56	38.20
20.		120.0	39.37	34.10	32.77	30.45
21.		83.4	36.27	31.17	30.08	28.75
22.		93.4	46.18	39.67	38.23	36.45
23.		124.1	59.58	48.98	46.64	43.77
24.		75.7	39.14	35.48	34.67	33.67

Table 3. Comparison of the group-contribution prediction of refractive index of conjugated polymers based on the molar-refraction tabulation in the literature and the present study

polymer	[a]nl_{589nm}	nl_{2500nm}	prediction [b]$(n_{LL})_{old}$	% error to nl_{589nm}	% error to nl_{2500nm}	$(n_{LL})_{new}$	% error to nl_{2500nm}
1. PPI	2.00	1.79	1.766	-11.7	-1.3	1.772	-1.0
2. PMPI	1.78	1.66	1.738	-2.4	+4.7	1.668	+0.5
3. PPI/PMPI	1.98	1.73	1.750	-11.6	+1.2	1.668	-0.9
4. PMOPI	1.86	1.66	1.622	-12.8	-2.3	1.666	+0.4
5. PHOPI	1.95	1.77	1.773	-9.1	+0.2	1.781	+0.6
6. MO-PPI	1.91	1.73	1.712	-10.4	-1.0	1.719	-0.6
7. P3MOPI	1.96	1.62	1.635	-16.6	+0.9	1.638	+1.1
8. MO-PHOPI	1.82	1.74	1.716	-5.7	-1.4	1.726	-0.8
9. PBPI	2.10	1.79	1.744	-17.0	-2.6	1.791	+0.1
10. PTMOPI	2.04	1.75	1.673	-18.0	-4.4	1.751	+0.2
11. PSPI	1.83	1.69	1.756	-4.0	+3.9	1.686	-0.2
12. PSMOPI	2.15	1.64	1.682	-21.8	+2.6	1.623	-1.0
13. PBEPI	1.88	1.76	1.721	-8.5	-2.2	1.757	-0.2
14. 1,5-PNI	2.24	1.79	1.774	-20.8	-0.9	1.817	+1.5
15. 1,5-PMONI	1.92	1.75	1.688	-12.1	-3.5	1.728	-1.2
16. PPPQ	1.75	1.69	1.627	-7.0	-3.7	1.696	+0.4
17. PBPQ	1.95	1.79	1.635	-16.2	-8.7	1.765	-1.4
18. PSPQ	1.97	1.79	1.641	-16.7	-12.2	1.832	-2.0
19. PBAPQ	2.05	1.87	1.641	-20.0	-7.8	1.776	-0.2
20. PTPQ	2.09	1.78	1.641	-21.5	-7.8	1.776	-0.2
21. PBTPQ	2.22	1.90	1.654	-25.5	-12.9	1.904	+0.2
22. PPDA	1.87	1.68	1.618	-13.5	-3.7	1.660	-1.2
23. PBDA	1.95	1.78	1.629	-16.5	-8.5	1.742	-2.1
24. PSDA	2.04	1.81	1.631	-20.0	-9.9	1.811	+0.1
25. PBADA	1.97	1.76	1.636	-17.0	-7.0	1.806	+2.6
26. PBZT	1.92	1.69	1.789	-6.8	+5.9	1.684	-0.4
27. PBTV	2.13	1.74	1.792	-15.9	+3.0	1.708	-1.8
28. PBTDV	2.24	1.85	1.757	-21.6	-5.0	1.799	-2.7
29. PBTPV	2.39	1.92	1.739	-27.2	-9.4	1.897	-1.4
30. 14PNBT	1.93	1.75	1.811	-6.2	+3.5	1.752	+0.1
31. PBIDV	2.20	1.82	1.704	-22.5	-6.4	1.789	-1.7
32. PBIPV	2.01	1.75	1.700	-15.4	-2.3	1.781	+1.8
33. PBO	2.04	1.70	1.721	-15.6	+1.2	1.692	-0.5
			average |% error|	= 14.8%	=4.6%		=0.9%

a. extrapolated refractive index by the three-term Sellmeier equation in Table 1.

b. based on the literature molar refraction data at 589 nm (sodium D line) (Ref. 15).

Table 4. Predicted isotropic refractive indices of several well-known π-conjugated polymers.

polymer	$n\|_{700\ nm}$	$n\|_{1064\ nm}$	$n\|_{1319\ nm}$	$n\|_{2500\ nm}$
trans-PA	—— [a]	2.47	2.43	2.44
PPV	2.28	2.04	2.00	1.95
DMO-PPV	1.99	1.78	1.74	1.70
PPP	2.13	1.97	1.93	1.89
PT	3.90	3.04	2.91	2.77
PTV	3.56	2.66	2.52	2.42

a. 700 nm is within the optical absorption band of *trans*-PA.

Figure Captions

Figure 1. The optical dispersion of molar refraction of *p*-phenylene (a), *p*-biphenylene (b), and *p*-terphenylene (c) functional groups.

Figure 2. The optical dispersion of molar refraction of the 2,5-thiophenediyl (a) and 2,2'-bithiophene-5,5'-diyl (b) functional groups.

Figure 3. The optical dispersion of molar refraction of the *trans*-vinylene (a) and *trans,trans*-divinylene (b) functional groups.

Figure 4. Dependence of the reduced molar refraction $(R_{LL}/(R_{LL})_0$ on the number of units (N). The dashed line is the reported scaling law in the literature (Ref. 36).

Figure 5. The optical dispersion of molar refraction of *p*-phenylene (a), 2-methyl-*p*-phenylene (b), 2-methoxy-*p*-phenylene (c), and 2,5-dimethoxy-*p*-phenylene (d) functional groups.

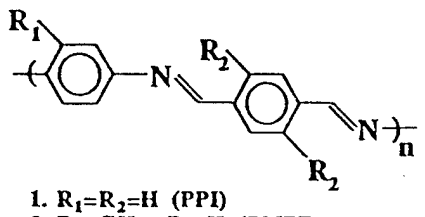
Figure 6. The optical dispersion of molar refraction of benzobisthiazole (a), benzobisoxazole (b), and benzobisimidazole (c) functional groups.

Figure 7. Predicted isotropic in-plane refractive indices (n_{TE}) of *trans*-polyacetylene (a), poly(*p*-phenylenevinylene) (b), poly(*p*-phenylene) (c), and poly(2,5-dimethoxy-1,4-phenylenevinylene) (d).

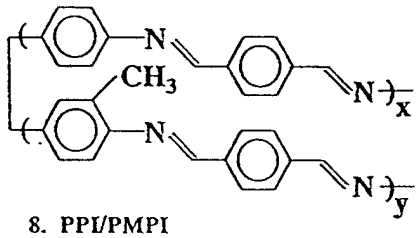
Figure 8. Predicted isotropic in-plane refractive indices (n_{TE}) of polythiophene (a) and poly(2,5-thienylene vinylene) (b).

Chart I

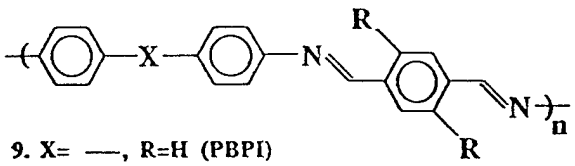
Polyimines



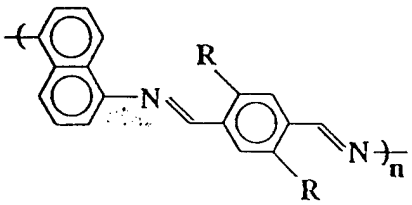
1. $R_1=R_2=H$ (PPI)
2. $R_1=CH_3$, $R_2=H$ (PMPI)
3. $R_1=H$, $R_2=OCH_3$ (PMOPI)
4. $R_1=H$, $R_2=OH$ (PHOPI)
5. $R_1=OCH_3$, $R_2=H$ (MO-PPI)
6. $R_1=R_2=OCH_3$ (P3MOPI)
7. $R_1=OCH_3$, $R_2=OH$ (MO-PHOPI)



8. PPI/PMPI

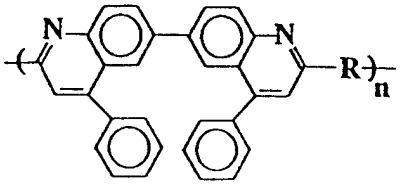


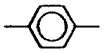
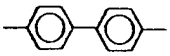
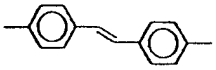
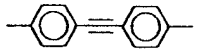
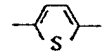
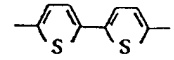
9. X= —, R=H (PBPI)
10. X=  , R=OCH_3 (PTMOPI)
11. X=  , R=H (PSPI)
12. X=  , R=OCH_3 (PSMOPI)
13. X= —O—, R=H (PBEPI)



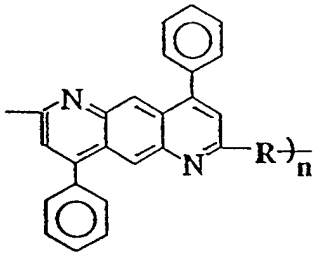
14. R=H (1,5-PNI)
15. R=OCH_3 (1,5-PMONI)

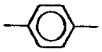
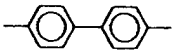
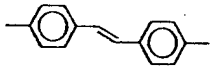
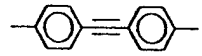
Polyquinolines



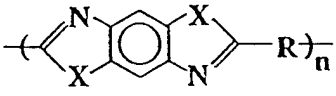
16. R=  (PPPQ)
17. R=  (PBPQ)
18. R=  (PSPQ)
19. R=  (PBAPQ)
20. R=  (PTPQ)
21. R=  (PBTPQ)

Polyanthrazolines



22. R=  (PPDA)
23. R=  (PBDA)
24. R=  (PSDA)
25. R=  (PBADA)

Polybenzobisazoles



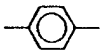
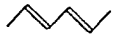
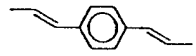
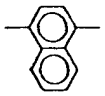
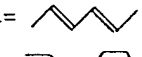
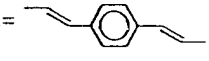
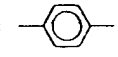
26. X=S, R=  (PBZT)
27. X=S, R=  (PBTV)
28. X=S, R=  (PBTDV)
29. X=S, R=  (PBTPV)
30. X=S, R=  (14PNBT)
31. X=NH, R=  (PBIDV)
32. X=NH, R=  (PBIPV)
33. X=O, R=  (PBO, X is *cis*)

Fig. 1

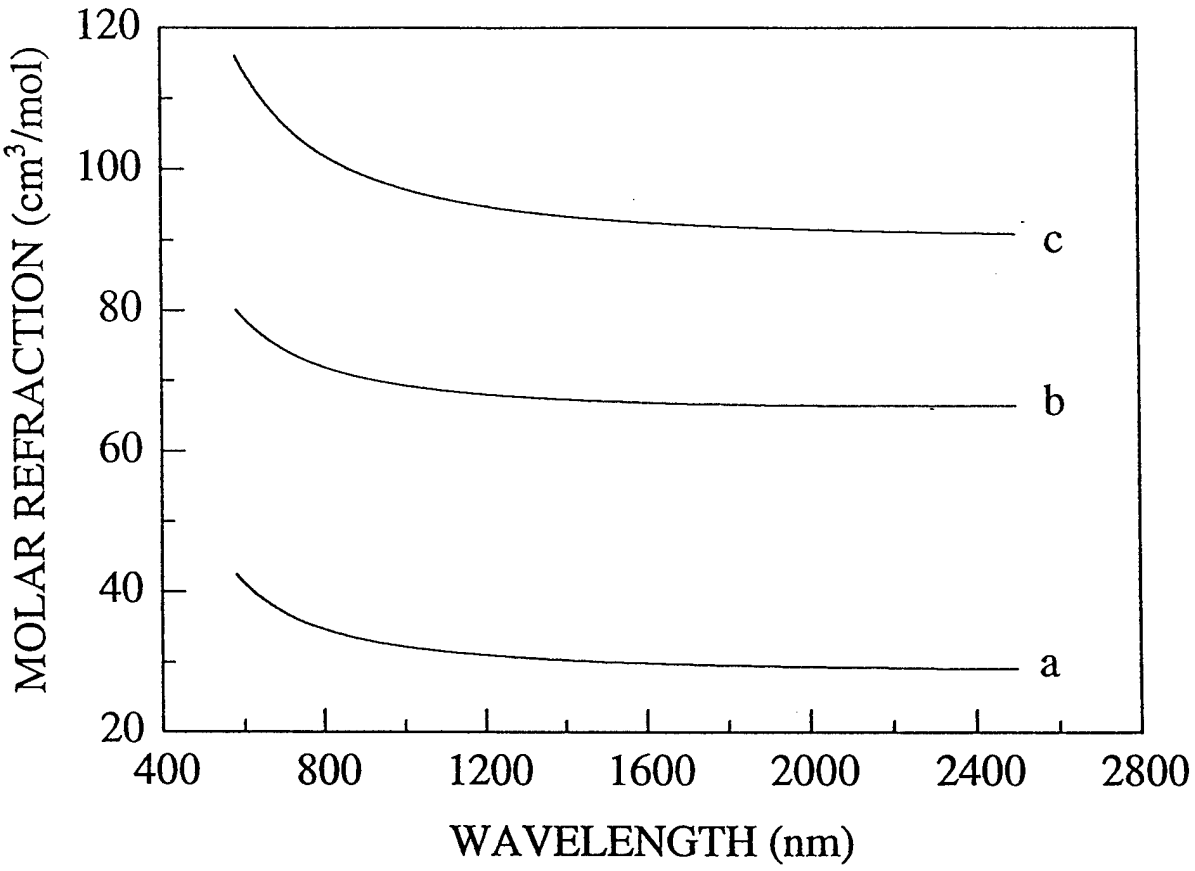

120
100
80
60
40
20
MOLAR REFRACTION (cm³/mol)
400
800
1200
1600
2000
2400
2800
WAVELENGTH (nm)
c
b
a

Fig. 2

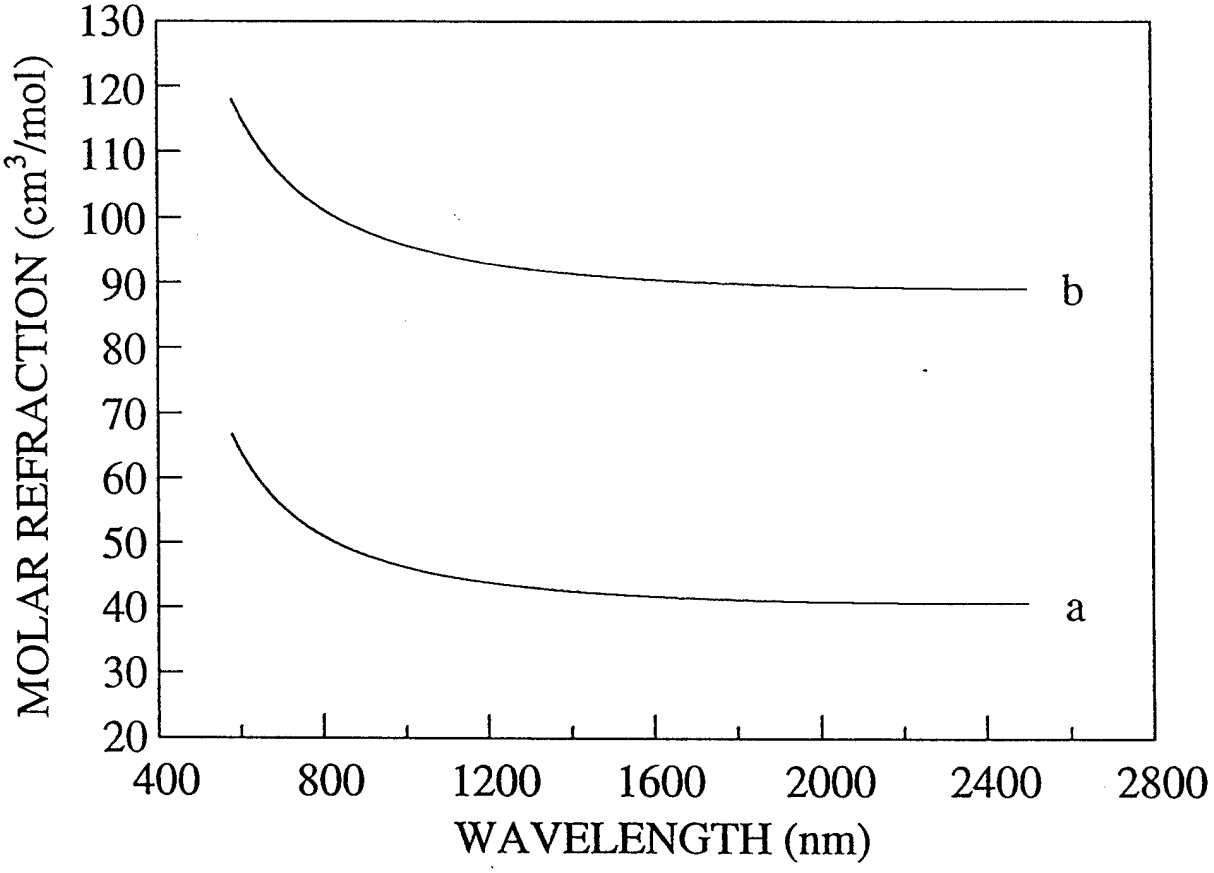

MOLAR REFRACTION (cm³/mol)
130
120
110
100
90
80
70
60
50
40
30
20
400
800
1200
1600
2000
2400
2800
WAVELENGTH (nm)
b
a

Fig. 3

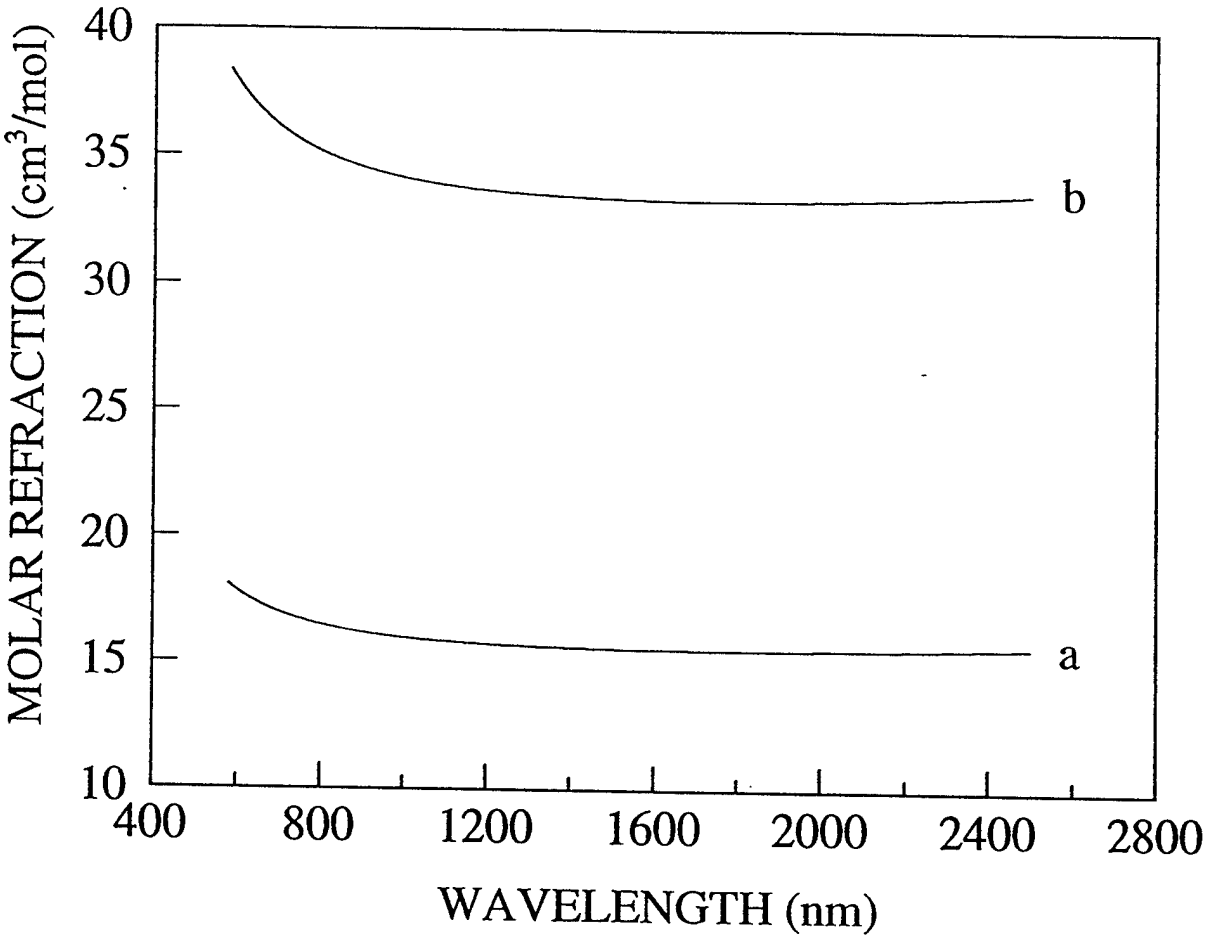

MOLAR REFRACTION (cm³/mol)
40
35
30
25
20
15
10
400
800
1200
1600
2000
2400
2800
WAVELENGTH (nm)
b
a

Fig. 4

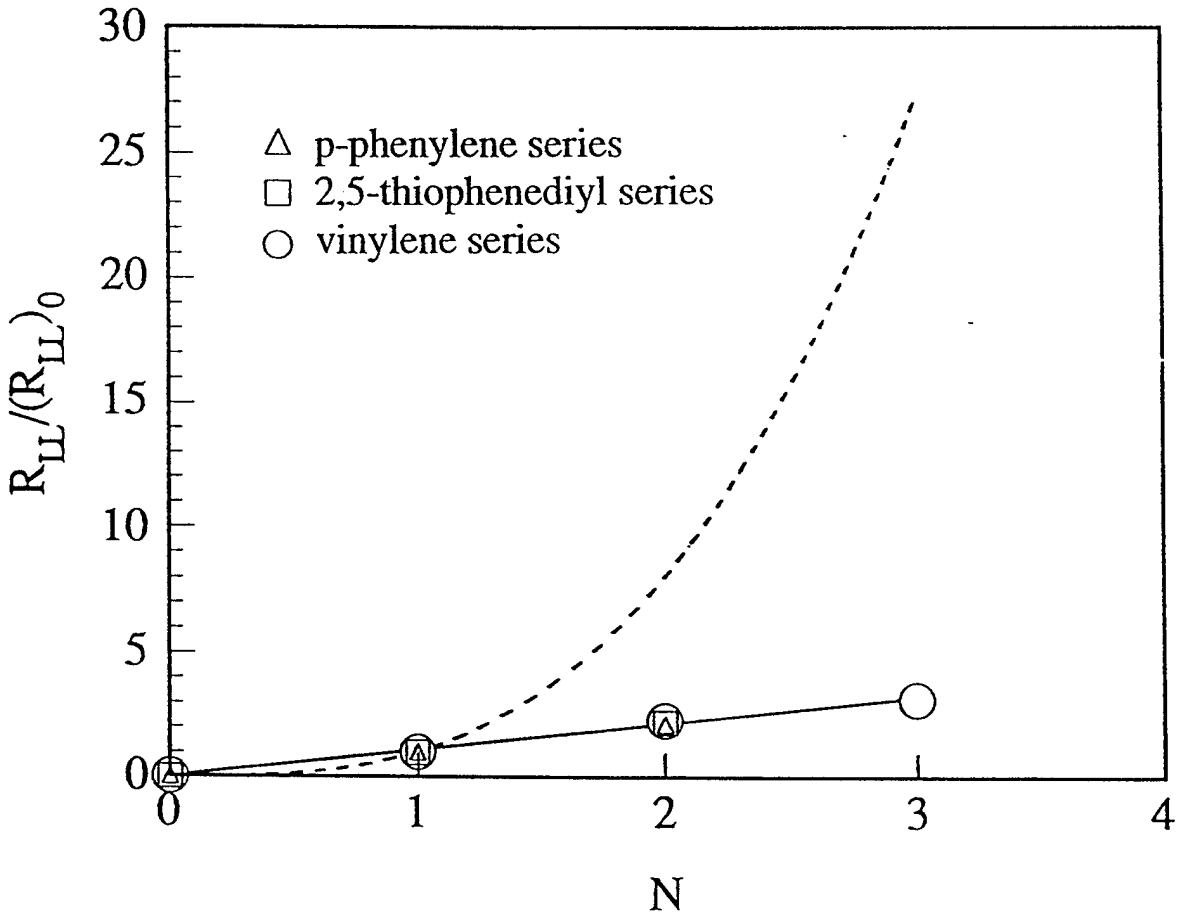

30
25
20
15
10
5
0
0
1
2
3
4
N
$R_{LL}/(R_{LL})_0$
△ p-phenylene series
□ 2,5-thiophenediyl series
○ vinylene series

Fig. 5

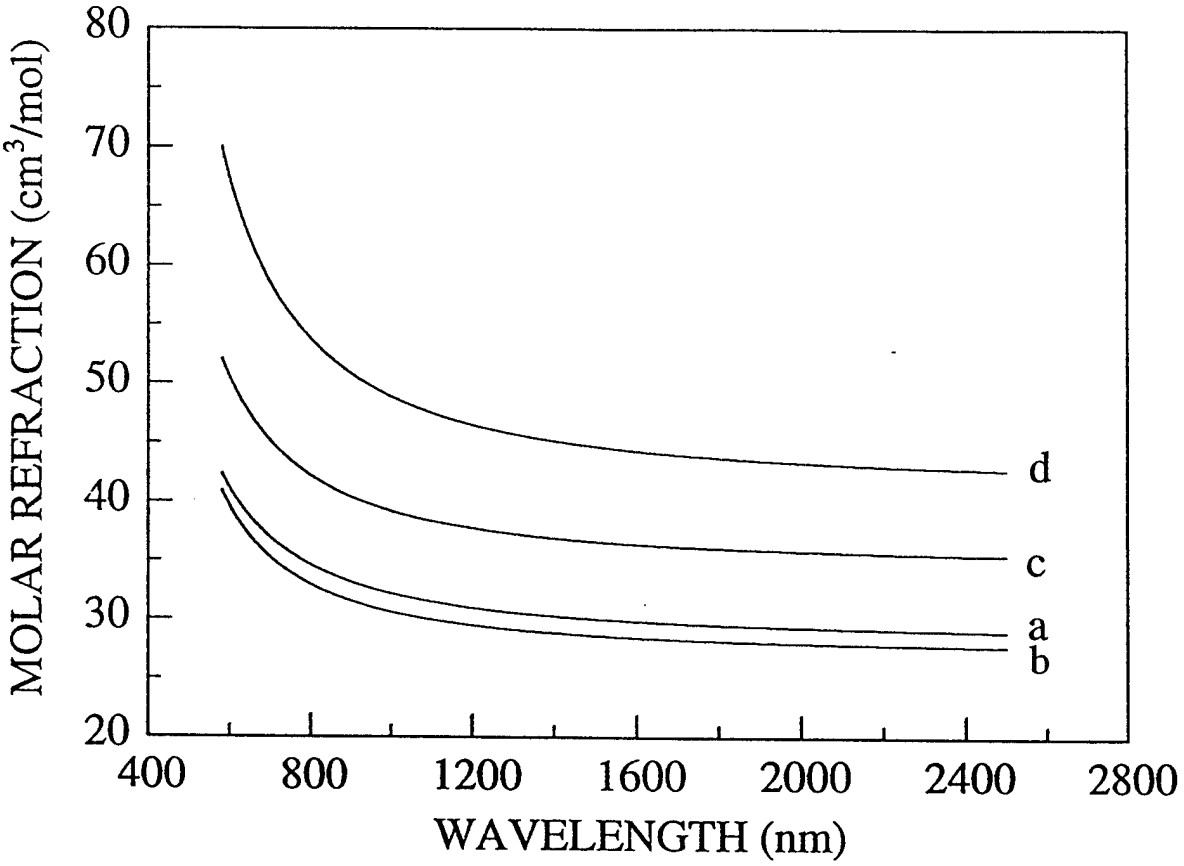

MOLAR REFRACTION (cm³/mol)
80
70
60
50
40
30
20
400
800
1200
1600
2000
2400
2800
WAVELENGTH (nm)
d
c
a
b

Fig. 6

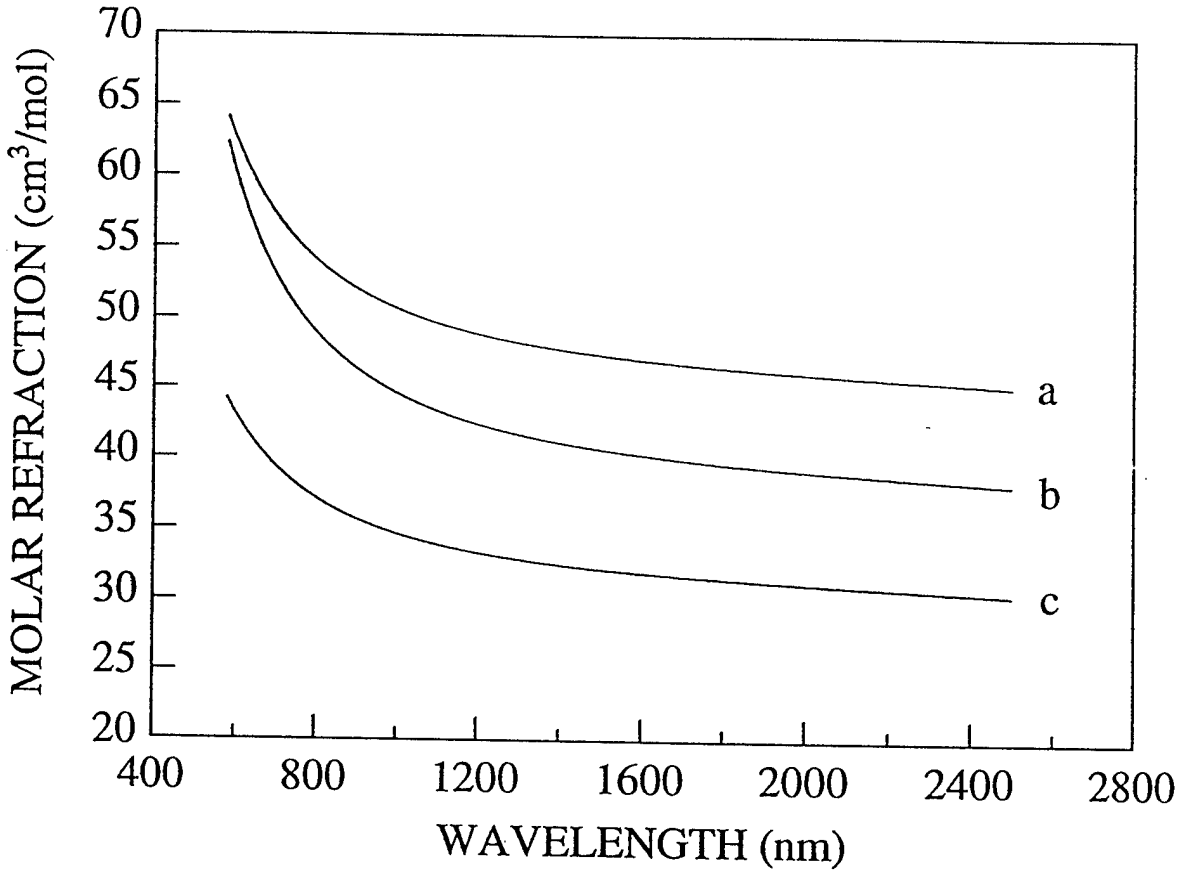

MOLAR REFRACTION (cm³/mol)
70
65
60
55
50
45
40
35
30
25
20
400
800
1200
1600
2000
2400
2800
WAVELENGTH (nm)
a
b
c

Fig. 7

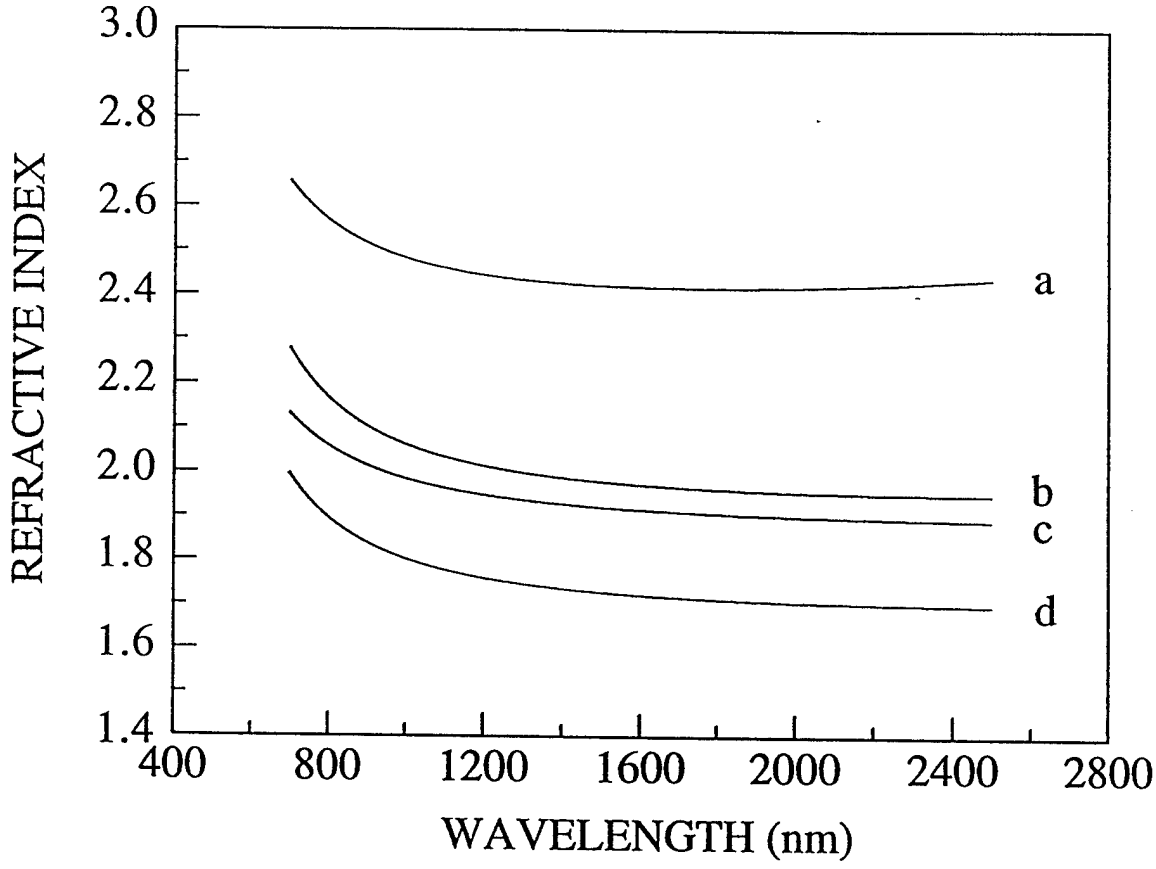
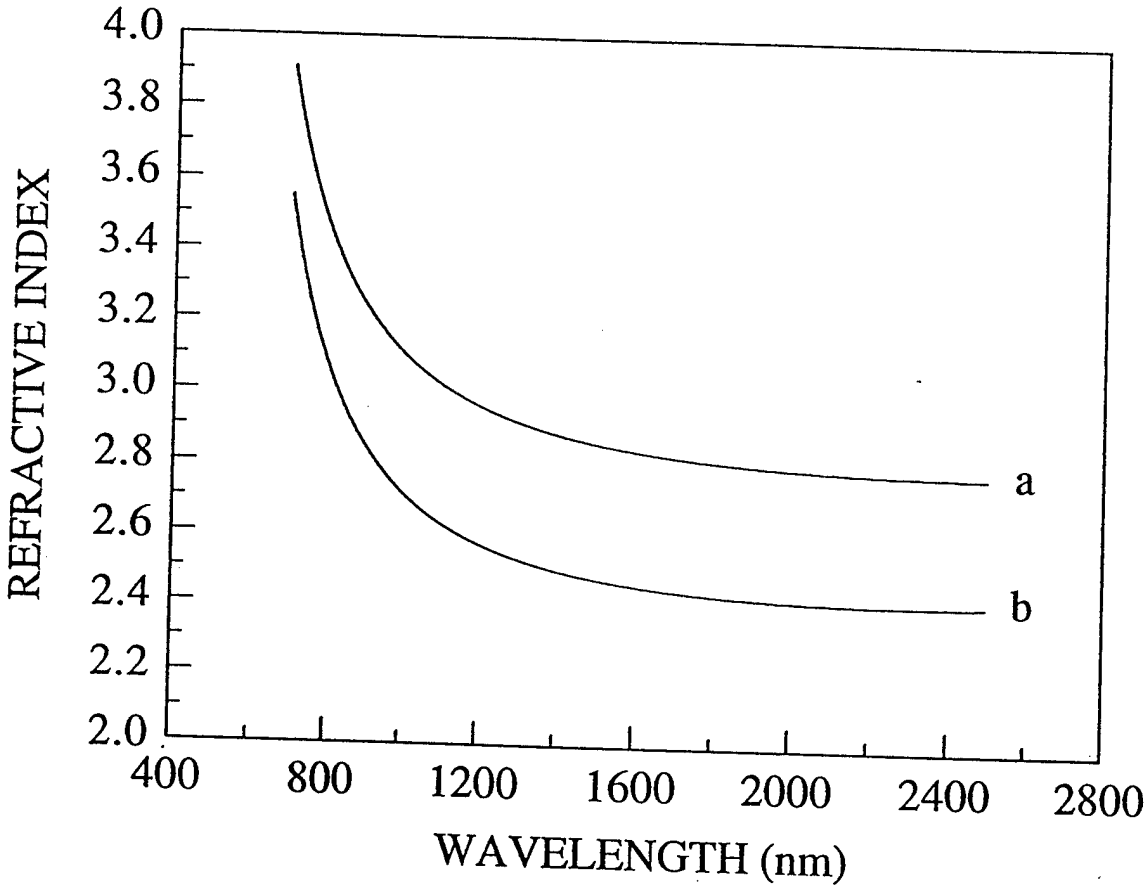

3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
REFRACTIVE INDEX
400
800
1200
1600
2000
2400
2800
WAVELENGTH (nm)
a
b
c
d

Fig. 8


4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
REFRACTIVE INDEX
400
800
1200
1600
2000
2400
2800
WAVELENGTH (nm)
a
b