Effects of Structure on Refractive Index of Conjugated Polyimines

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Received September 27, 1993. Revised Manuscript Received November 29, 1993®

The optical dispersion of the isotropic refractive index of 14 conjugated polyimines has been measured in the 700–2500-nm wavelength range and used to investigate the effects of molecular structure on the refractive index of π-conjugated polymers. The measured refractive index dispersion data were found to be described well by a three-term Sellmeier equation. A modified Abbe number based on data at 1064, 1319, and 2500 nm is suggested as a numerical measure of the degree of refractive index dispersion in the nonabsorbing wavelength region of conjugated polymers. Off-resonance at 2500 nm, the refractive index was in the range of 1.79 for the parent conjugated polyimine poly(1,4-phenylenemethylidynenitrilo-1,4-phenylenenitrilomethylidyne) to 1.62 for the trimethoxy-substituted derivative poly(2,5-dimethoxy-1,4-phenylenemethylidynenitrilo-2-methoxy-1,4-phenylenenitrilomethylidyne). The structure–refractive index relationships in these π-conjugated polymers were accounted for by the competing effects of *polarizability* and *molar volume* on the refractive index. A comparison between the present data and various chemical group-contribution models based on existing tabulated group molar refractions at 589 nm shows that these tabulated values are unsatisfactory for predicting the refractive indices of π-conjugated polymers.

Introduction

Polymers with low optical transmission loss and minimal wavelength dispersion of refractive index are currently of research interest due to their applications in plastic optical fibers.[1,2] Compared to the predominant inorganic glass fibers, polymers provide the advantages of light weight, good ductility, large core diameter, and high numerical aperture. Most importantly, synthetic polymer chemistry techniques also make material tailorability possible. Structural modifications in plastic optical fibers such as inclusion of fluorine atoms to decrease the refractive index and replacement of hydrogen atoms with deuterium atoms to shift the optical window have been developed to further increase the compatability of polymers with optical communication applications.[3,4]

Besides their applications in passive light waveguides and optical interconnection, polymers are also emerging as active elements in light-emitting diodes,[5–7] photodetectors, and optical switching and information processing.[8–10] Recent research advances in nonlinear optical polymers have shown high nonresonant third-order optical susceptibility in conjugated polymers such as polyacetylene,[11] poly(diacetylene),[12] poly(*p*-phenylenevinylenes),[13] poly(*p*-phenylenebenzobisthiazoles),[14] polyquinolines,[15] polyanilines,[16] and polyimines.[17] Important future directions of research in the field of photonic polymers include exploitation of the nonlinear optical properties of conjugated polymers in various photonic devices, and this requires suitable processing techniques that will facilitate the fabrication of optical-quality and low-loss thin films and fibers. Initial efforts in this area have resulted in the demonstration of conjugated polymer waveguide devices.[18,19]

To realize the potential of polymers in optoelectronic and photonic applications, it is essential to have infor-

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® Abstract published in *Advance ACS Abstracts*, January 1, 1994.

(1) Hornak, L. A., Ed. *Polymers for Lightwave And Integrated Optics: Technology and Applications*; Marcel Dekker: New York, 1992.

(2) Musikant, S. *Optical Materials: An Introduction to Selection And Application*; Marcel Dekker: New York, 1985.

(3) Kaino, T. In ref 1, pp 1–38.

(4) Kaino, T. In *Frontiers of Macromolecular Science*; Saegusa, T., Higashimura, T., Abe, A., Eds.; Blackwell: London, 1989; pp 475–480.

(5) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539. (b) Bradley, D. D. C. *Adv. Mater.* **1992**, *4*, 756.

(6) (a) Braum, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982. (b) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature (London)* **1992**, *357*, 477.

(7) (a) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 4726. (b) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules*, in press.

(8) Jenekhe, S. A., Ed. *Macromolecular Host-Guest Complex: Optical, Optoelectronic, And Photorefractive Properties And Applications*; Materials Research Society Proceedings; MRS: Pittsburgh, 1992; Vol. 277.

(9) Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; *Materials For Nonlinear Optics: Chemical Perspectives*; American Chemical Society: Washington, DC, 1991.

(10) Prasad, P. N.; Williams, D. J. *An Introduction to Nonlinear Optical Effects in Molecules And Polymers*; John Wiley: New York, 1991.

(11) Fann, W.-S.; Benson, S.; Madey, J. M. J.; Etemad, S.; Baker, G. L.; Kajzar, F. *Phys. Rev. Lett.* **1989**, *62*, 1492.

(12) Kanetake, T.; Ishikawa, K.; Hasegawa, T.; Koda, T.; Takeda, K.; Hasegawa, M.; Kubodera, K.; Kobayashi, H. *Appl. Phys. Lett.* **1989**, *54*, 2287.

(13) Singh, B. P.; Prasad, P. N.; Karasz, F. E. *Polymer* **1988**, *29*, 1940.

(14) Vanherzeele, H.; Meth, J. S.; Jenekhe, S. A.; Roberts, M. F. *J. Opt. Soc. Am.* **1992**, *B9*, 524.

(15) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, M.; Meth, J. S. *J. Phys. Chem.* **1992**, *96*, 2837.

(16) Osaheni, J. A.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S.; Sun, Y.; MacDiarmid, A. G. *J. Phys. Chem.* **1992**, *96*, 2830.

(17) (a) Jenekhe, S. A.; Yang, C. J.; Vanherzeele, H.; Meth, J. S. *Chem. Mater.* **1991**, *3*, 985. (b) Yang, C. J.; Jenekhe, S. A.; Meth, J. S.; Vanherzeele, H. *Mater. Res. Soc. Proc.* **1992**, *247*, 247. (c) Yang, C. J.; Jenekhe, S. A.; Meth, J. S.; Vanherzeele, H. *Polym. Adv. Technol.*, in press.

(18) Mittler-Neher, S.; Otomo, A.; Stegeman, G. I.; Lee, C. Y.-C.; Mehta, R.; Agrawal, A. K.; Jenekhe, S. A. *Appl. Phys. Lett.* **1993**, *62*, 115.

(19) (a) Thakur, M.; Frye, R.; Greene, B. *Appl. Phys. Lett.* **1990**, *56*, 1187. (b) Thakur, M.; Krol, D. M. *Appl. Phys. Lett.* **1990**, *56*, 1213.

0897-4756/94/2806-0196$04.50/0

mation about the basic optical properties of the materials such as the refractive index. In contrast to the abundant data on the refractive index of *nonconjugated* polymers,[20-22] there are only few literature reports on the refractive index of *conjugated* polymers.[23,24] The large data base on the linear optical properties of nonconjugated polymers not only provides the refractive index data for vast amounts of molecular structures[20-22] but has also led to the development of a reliable group contribution computation scheme that can be used to predict the refractive indices of organic polymers.[21,22] However, the current group contribution prediction of the refractive indexes of polymers[22] deviates significantly from the refractive index data when applied to some π-conjugated polymers.[23] It is therefore very important to measure the refractive index of conjugated polymers and understand the underlying structure–property relationships. Furthermore, the frequency dispersion of the refractive index must also be known, especially in π-conjugated polymers in which optical properties can be highly dispersive. Such information on the frequency dispersion of the refractive index and the effects of molecular structure are very important to the application of conjugated polymers in photonic technologies, including passive waveguide devices and nonlinear optical devices.

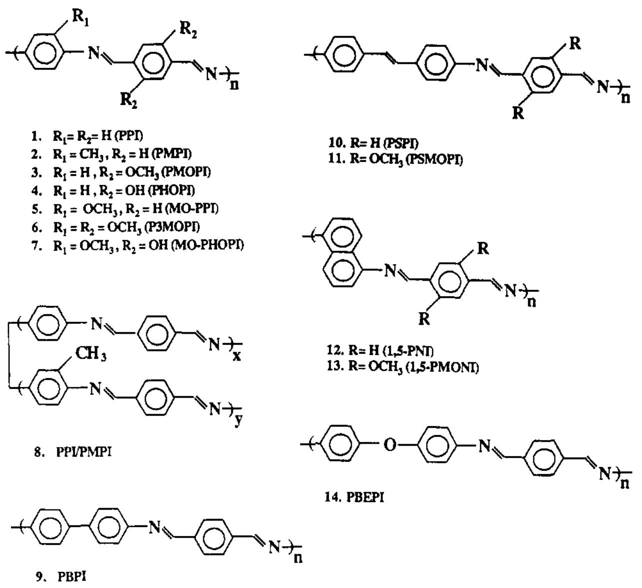
We recently reported the synthesis, characterization, solution processing, and the third-order nonlinear optical properties of a series of conjugated aromatic polyimines.[17,25] In this paper, we report studies of the wavelength dispersion of the refractive index, in the wavelength range 0.7–2.5 μm, of 14 conjugated polyimines with various backbone and side-group substitution structures. The refractive index data are fitted with the Sellmeier dispersion formula to provide facile and accurate interpolation in the transparent wavelength range. The structures of the polyimines, shown in Chart 1, include *p*-phenylene, *p*-biphenylene, 1,5-naphthalene, vinylene, and ether linkages in the polymer backbone, and methyl, methoxy, and hydroxy side-group substitutions. The diverse molecular structures in the present study are designed to provide information on the effects of structure on the refractive index of conjugated polymers. Computational studies on the functional group contributions to the molar refraction of conjugated polymers that include different classes of π-conjugated polymers are currently in progress and will be reported elsewhere.

Experimental Section

Materials. All the polymers were synthesized by reacting aromatic diamines with aromatic dialdehydes in 1:1 hexamethylenephosphoramide/*N*-methylpyrrolidinone in the presence of water-adsorbing lithium chloride. The details of the synthesis and characterization of these polymers are described elsewhere.[25]

Preparation of Thin Films. The processing of conjugated polyimines into thin films via the soluble coordinational complexes has been reported in our earlier studies.[25] Thin films of the polymers on fused silica substrates were prepared by spin coating concentrated solutions (5–7 wt %) of the polymers complexed with gallium chloride or diaryl phosphate in nitromethane or *m*-cresol, respectively.[25] The resulting films of the polymer complexes were decomplexed, in water in the case of $GaCl_3$ complexes or trialkylamine/ethanol in the case of diaryl phosphate complexes, to produce amorphous thin films of the pure polymers as previously described.[25] To control the morphology of the polymer films, the molar ratio of the imine nitrogen to the complexation reagent was kept as 2:1, the ratio at which the solid complexes have been shown to be completely amorphous.[26] The film thickness measured with an α-step profilometer was in the range 1.0–4.0 μm. In a 2000-μm scan of linear distance with the α-step profilometer, the variation of film thickness was less than 1%.

Chart 1



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. PBPI

10. R= H (PSPI)
11. R= OCH_3 (PSMOPI)

12. R= H (1,5-PNI)
13. R= OCH_3 (1,5-PMONI)

14. PBEPI

Transmission Spectra. Transmission spectra of thin films of the polymers were 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 films. The slit of the instrument was set at 1 nm.

Refractive Index. The refractive index was deduced from the interference fringes in the transmission spectra.[27,28] This technique was developed by Manafacier et al. and further modified by Swanepoel.[27,28] In this method, the consecutive wavelengths at which the maximal and minimal transmission occurred are measured. The consecutive λ_{max}'s and λ_{min}'s are then used as input to a computer program which iterates within a preset tolerance to give the approximate order numbers by applying nonlinear regression of the following equation to the data:[27]

$$\frac{\lambda\lambda'}{2(\lambda - \lambda')} = \frac{D}{\lambda^y} + C \qquad (1)$$

λ and λ' are two adjacent wavelengths (nanometers) where the transmission maximum or minimum occurs. C, D, and y are parameters to be determined by nonlinear regression. The approximate value of m at each transmission extremum is given by

$$m \approx C/\lambda \qquad (2)$$

The actual value of the order number is an integer of a half-integer for each transmission maximum or minimum, respectively. The wavelength dispersion of refractive index is then obtained

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(20) Bicerano, J. *Prediction of Polymer Properties*; Marcel Dekker: New York, 1993.

(21) Seferis, J. C. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; Vols. VI/451–VI/461.

(22) Van Krevelen, D. W. *Properties of Polymers: Their Estimation And Correlation with Chemical Structure*; Elsevier: Amsterdam, 1976.

(23) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1992**, *4*, 95.

(24) Mattoussi, H.; Scrinivasarao, M.; Kaatz, P. G.; Berry, G. C. *Macromolecules* **1992**, *25*, 2860.

(25) (a) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* **1991**, *3*, 878. (b) Yang, C. J.; Jenekhe, S. A., manuscript in preparation.

(26) Yang, C. J.; Jenekhe, S. A. *Mater. Res. Soc. Proc.* **1992**, *277*, 197.

(27) (a) Manifacier, J. C.; Gasiot, J.; Fillard, J. P. *J. Phys. E: Sci. Instrum.* **1976**, *9*, 1002. (b) Manifacier, J. C.; DE Murcia, M.; Fillard, J. P. *Thin Solid Films* **1977**, *41*, 127.

(28) Swanepoel, R. *J. Opt. Soc. Am.* **1985**, *A2*, 1339.

by the following equation in which d is the film thickness:

$$n = m\lambda/2d \tag{3}$$

Sellmeier Dispersion Formula.[29] It has been shown in numerous tabulated refractive index data sources that Sellmeier equation is suitable for accurately fitting the wavelength dispersion of the refractive index not only of inorganic glass and nonglass materials but also of organic molecules and polymers.[24,30-33] The success of the Sellmeier equation in this regard is due in part to its origin from a physical model, namely, the Lorentz oscillator model.[29a] Although not all materials can be adequately described by the Lorentz oscillator model, by including many oscillators through summations in this equation, the dispersion of the refractive index in the transparent regions (λ > absorption edge) can be modeled. The physical justification of the Sellmeier equation has been described extensively in the literature.[29a] Here, we use only the final form of this equation:

$$n^2 = 1 + \sum_{s=1} \frac{a_s\lambda^2}{\lambda^2 - b_s^{\,2}} \tag{4}$$

where n is refractive index, λ is wavelength in micrometers, a_s is a constant relating to the oscillator strength, and b_s is the resonance wavelength (in micrometers) of the refractive index. A three-term Sellmeier equation was used to fit our refractive index data. Due to the complexity of solving a set of nonlinear equations, judicous initial guesses of a_s and b_s are required to obtain convergent results with physically reasonable values. In our programmed computation, the one-term Sellmeier equation was first used to fit several data points at short-wavelength regions, then the resulting resonance wavelength value (i.e., b_s) was used as the starting value in the subsequent three-term Sellmeier equation fit of all the data points. Specifically, two starting b_s values in the three-term Sellmeier equation were set at the resonance wavelength obtained from the one-term Sellmeier equation fit and at half of this value, and the third b_s value was guessed initially as 0.4 or 0.5 μm, or double the longest wavelength used in the experiment. The latter initial guess has been suggested in fitting the refractive index data of inorganic glasses and semiconductors.[31]

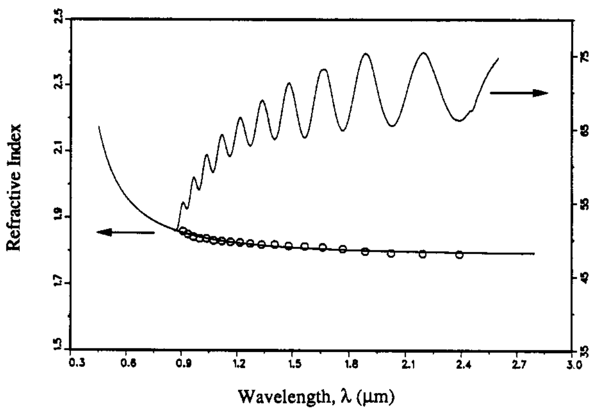

Figure 1. Optical transmission spectrum and the refractive index dispersion data of PPI.

Table 1. Order Number and Refractive Index of PPI

λ, nm	$m_{\text{calculated}} = C/\lambda$	m	$n = m\lambda/2d$
2390.1	5.5	5.5	1.791
2192.1	6.0	6.0	1.792
2025.6	6.5	6.5	1.794
1886.5	7.0	7.0	1.799
1767.4	7.5	7.5	1.806
1661.5	7.9	8.0	1.811
1566.1	8.4	8.5	1.814
1480.2	8.9	9.0	1.815
1405.5	9.4	9.5	1.819
1335.0	9.9	10.0	1.819
1273.3	10.4	10.5	1.822
1217.5	10.8	11.0	1.825
1166.3	11.3	11.5	1.827
1119.1	11.8	12.0	1.830
1075.3	12.3	12.5	1.831
1037.0	12.7	13.0	1.837
998.5	13.2	13.5	1.837
965.9	13.7	14.0	1.842
936.4	14.1	14.5	1.850
909.7	14.6	15.0	1.859

Results and Discussion

Measurement of $n(\lambda)$ and Sellmeier Equation Fit of Data. The wavelength dispersion of the refractive index was determined using the interference fringes in the transmission spectrum coupled with the data analysis provided by the Swanepoel method.[28] Instead of measuring the transmission extrema ($T_{\max}$, $T_{\min}$) and wavelengths corresponding to these extrema as described by Manafacier et al.,[27] in the Swanepoel method only the wavelengths are measured to calculate the refractive index. This is especially advantageous in low refractive index materials such as organic polymers which exhibit only small differences between $T_{\max}$ and $T_{\min}$, and consequently deduction of refractive index from $T_{\max}$ and $T_{\min}$ may give erroneous values. An arguable point about the applicability of the Swanepoel method arises from the inclusion of a simple empirical dispersion formula (i.e., $n^2 = a/\lambda^x + b$) in the computation scheme.[28] Actual material behavior may not reflect this simple type of wavelength dispersion. However, the accuracy of the refractive index determined by the method can still be guaranteed because only an estimation of the order number m is made from the least-squares fit. The estimated m is then rounded off to an integer or a half-integer, followed by the determination of refractive index according to $n = m\lambda/2d$ which is an exact relationship for the constructive or destructive interference, depending on whether a transmission maximum or minimum is observed.

Figure 1 illustrates an example of the interference fringes in the transmission spectrum of a conjugated polyimine. The polymer is PPI with a film thickness of 3.67 μm. At wavelengths longer than about 2.7 μm, the interference fringe pattern is obscured by the molecular vibrational absorption in this region. The wavelength values at which transmission extrema occur in the transmission spectrum of Figure 1 were used as input to a programmed nonlinear regression computation to calculate fitting parameters C, D, and y according to eq 1. The results of the fitting are $D = 3.30 \times 10^{11}$, $C = 1.32 \times 10^4$, and $y = 2.78$. The value of the parameter C was then used to calculate the order number m at each transmission extremum. Table 1 shows the calculated order numbers and the corresponding refractive indices. The optical quality of the polymer film is a major factor in obtaining a good interference fringe pattern. Also, it was found that a film thickness of more than 1 μm is required to provide sufficient and unambiguous interference fringes. As shown in Figure 1, the interference fringes of a 3.67-μm PPI film show 20 clear maximal and minimal transmission from which the corresponding wavelength is determined accurately. The order number was calculated to be 5.5 at the 2390.1-nm

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(29) (a) Ditchburn, R. W. *Light*, 2nd ed.; Interscience: New York, 1963; pp 562–567. (b) Sellmeier, W. *Pogg. Ann. Bd.* **1871**, *143*, S. 272.

(30) Grossman, C. H.; Garito, A. F. *Mol. Cryst. Liq. Cryst.* **1989**, *168*, 255.

(31) Tatian, B. *Appl. Opt.* **1984**, *23*, 4477.

(32) Li, H. H. *J. Phys. Chem. Ref. Data* **1976**, *5*, 329.

(33) Debenham, M. *Appl. Opt.* **1984**, *23*, 2238.

Table 2. Fitting Parameters of the Sellmeier Equation for Polyimines[a]

polymer	a_1 b_1	a_2 b_2	a_3 b_3
PPI	0.0006 ± 2.0E–5 0.3059 ± 4.0E–5	2.1697 ± 4.0E–4 0.3061 ± 2.0E–5	0.0072 ± 3.0E–5 0.3056 ± 1.0E–5
PMPI	0.0276 ± 2.0E–4 0.2586 ± 2.0E–4	0.0690 ± 1.5E–3 0.2581 ± 8.0E–4	1.6511 ± 1.1E–3 0.2625 ± 1.0E–4
PPI/PMPI	0.7395 ± 1.2E–3 0.4033 ± 4.0E–4	0.5271 ± 2.6E–3 0.2464 ± 2.0E–4	0.6946 ± 1.9E–3 0.2705 ± 1.6E–3
PMOPI	1.7129 ± 9.0E–4 0.3221 ± 1.0E–4	0.0004 ± 7.0E–5 0.3205 ± 1.0E–4	0.0039 ± 4.0E–5 0.3197 ± 1.0E–4
PHOPI	2.0353 ± 3.2E–3 0.2902 ± 2.0E–4	0.0513 ± 1.3E–3 0.2932 ± 2.0E–4	0.0237 ± 1.0E–4 0.2929 ± 8.0E–4
MO-PPI	1.8896 ± 3.1E–3 0.2967 ± 3.0E–5	0.0201 ± 2.4E–3 0.2986 ± 1.0E–4	0.0652 ± 2.5E–3 0.2989 ± 1.0E–4
P3MOPI	0.0301 ± 6.0E–4 0.3908 ± 1.0E–4	1.5423 ± 6.0E–4 0.3883 ± 1.0E–5	0.0233 ± 4.0E–4 0.3907 ± 1.0E–4
MO-PHOPI	0.8207 ± 1.1E–2 0.1251 ± 3.6E–3	0.6652 ± 8.9E–3 0.2473 ± 1.0E–3	0.5138 ± 6.4E–3 0.2735 ± 1.9E–3
PBPI	2.0980 ± 4.9E–3 0.3549 ± 1.0E–4	0.0026 ± 3.0E–4 0.3558 ± 1.0E–4	0.0598 ± 3.0E–3 0.3561 ± 4.0E–4
PSPI	0.6529 ± 5.2E–3 0.2354 ± 8.0E–4	0.7698 ± 4.5E–3 0.1723 ± 2.0E–3	0.4207 ± 2.3E–3 0.3795 ± 9.0E–4
PSMOPI	1.4778 ± 2.4E–3 0.4351 ± 2.0E–4	0.0444 ± 1.9E–3 0.4495 ± 2.0E–4	0.1077 ± 1.9E–3 0.4512 ± 7.0E–4
1,5-PNI	0.4195 ± 1.4E–3 0.4091 ± 1.0E–4	0.0381 ± 1.1E–3 0.4084 ± 2.0E–4	1.7027 ± 1.3E–3 0.3993 ± 1.0E–4
1,5-PMONI	0.7110 ± 1.3E–3 0.2969 ± 1.0E–4	1.0084 ± 1.2E–3 0.2589 ± 2.0E–4	0.3280 ± 7.0E–4 0.3359 ± 2.0E–4
PBEPI	2.0049 ± 4.0E–4 0.2553 ± 2.0E–5	0.0152 ± 1.0E–4 0.2572 ± 1.0E–4	0.0464 ± 3.0E–4 0.2576 ± 1.0E–4

[a] b_1, b_2, and b_3 are in micrometers.

transmission minimum and was increased by a half-integer at each successive transmission extremum toward the short wavelength (Table 1). The corresponding refractive index of PPI increases from 1.79 at 2390.1 nm to 1.86 at a wavelength of 909.7 nm (Table 1).

Also shown in Figure 1 is the wavelength dispersion of the refractive index of PPI and the three-term Sellmeier equation fit of the data. The fitting parameters for the refractive index dispersion data of PPI and the other polymers in Chart 1 are collected in Table 2. A good agreement was obtained between the fittings and the experimental dispersion data, indicating the adequacy of fitting the refractive index data of conjugated polymers by the Sellmeier equation. In fitting these data, it was necessary to impose a nonnegative bound on numerical values. This restriction on computed a_s and b_s was imposed to retain the physical meaning. Unlike the Sellmeier equation fitting of inorganic glasses and semiconductors which exhibit b_s values in the far-IR range,[31] all the resonance wavelength values (b_s) in this study lie in the 0.15–0.45-μm range which corresponds reasonably to the electronic absorption of these polymers. The resulting Sellmeier equation parameters in Table 2 can be used to readily calculate the refractive index of the series of polyimines in the transparent region and thus they provide a convenient way to summarize the wavelength dispersion data of the refractive indices of these conjugated polymers.

Effects of Polymer Molecular Structure. The 14 polyimines in Chart 1 provide structural diversity that can be used to elucidate the structure–refractive index relationships in this class of conjugated polymers if we assume that the effects of morphology are negligible. The morphology of a semicrystalline polymer solid can influence its refractive index through two main factors: (i) degree of crystallinity and resultant density differences; (ii) chain orientation and related optical anisotropy.

Table 3. Optical Absorption Edge E_g, Molar Volume V, Selected Refractive Indices, and the Modified Abbe Number, ν_d', of Conjugated Polyimines

polymer	E_g (nm)	E_g (eV)	V (cm^3/mol)	$n_{1064\ \mathrm{nm}}$	$n_{1319\ \mathrm{nm}}$	$n_{2500\ \mathrm{nm}}$	ν_d'
PPI	496	2.50	161.9	1.84	1.82	1.79	16.40
PMPI	497	2.49	179.8	1.69	1.68	1.66	22.67
PPI/PMPI	497	2.49	170.9	1.78	1.76	1.73	15.20
PMOPI	529	2.34	220.5	1.70	1.68	1.66	17.00
PHOPI	600	2.07	171.1	1.81	1.79	1.77	19.75
MO-PPI	515	2.41	189.8	1.77	1.76	1.73	19.00
P3MOPI	555	2.23	248.4	1.69	1.66	1.62	9.43
MO-PHOPI	610	2.03	200.0	1.76	1.75	1.74	37.50
PBPI	490	2.53	227.4	1.85	1.82	1.79	13.67
PSPI	520	2.38	246.3	1.72	1.71	1.69	23.67
PSMOPI	540	2.30	304.9	1.72	1.68	1.64	8.50
1,5-PNI	495	2.51	215.4	1.88	1.84	1.79	9.33
1,5-PMONI	510	2.43	274.0	1.79	1.77	1.75	19.25
PBEPI	438	2.83	237.4	1.79	1.77	1.76	25.67

Although some of the polyimines without side-group substitutions have some amount of crystallinity as-synthesized, it was possible to obtain amorphous materials through the complexation-mediated processing of thin films.[25,26] In fact, all the films were carefully prepared under the same general conditions (e.g., spin coating of the soluble complexes, regeneration in nonsolvent, and drying) and only films with good optical quality, as judged by transparency in the visible and the ability to obtain good interference fringes, were used in refractive index measurements. That the assumption of negligible effects of morphology is reasonable was confirmed by the ability to reproduce the same refractive index dispersion data on different films of the same polymer prepared at different times from different solutions. Thus, all films of the polyimines investigated can be regarded as amorphous and isotropic materials, and the observed differences in the refractive index data reflect their molecular structures.

To facilitate the discussion of the effects of molecular structure and comparison between the 14 polyimines in Chart 1, the refractive index dispersion data will be graphically displayed for selected groups of the materials. Also, Table 3 shows the optical absorption edge or bandgap E_g and the refractive indices of all the polyimines at selected wavelengths (1064, 1319, and 2500 nm). The interplay of two key molecular parameters—*polarizability* α and *molar volume* V—in the structure–refractive index relationships of polyimines can be examined with respect to the structural variations such as *backbone structure, side-group substitutions, random copolymerization, and heteroatoms.* These two molecular parameters arise in the Lorentz–Lorenz theoretical model[34] of refractive index:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N_A \alpha}{3V} \tag{5}$$

in which N_A is the Avogadro's number. Thus refractive index decreases with increasing molar volume V (cm^3/mol) and increases with increasing polarizability α (cm^3). For a given polymer structure the repeat unit molar volume can be very accurately calculated by the group contribution method[22] and such values are given in Table 3 for the series of polyimines. The dominant contribution to the polarizability of a conjugated polymer comes from π-electron delocalization and various theoretical models[35] have established that $\alpha \sim L_d^3 \sim E_g^{-3}$, where L_d is the electronic

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(34) Boyd, R. W. *Nonlinear Optics*; Academic Press: San Diego, 1992; pp 148–151.

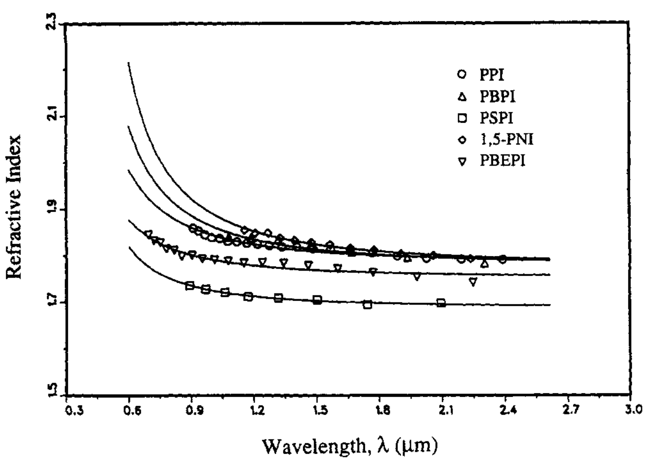

Figure 2. Refractive index dispersion data of PPI, PBPI, PSPI, PBEPI, and 1,5-PNI and their Sellmeier equation fit.

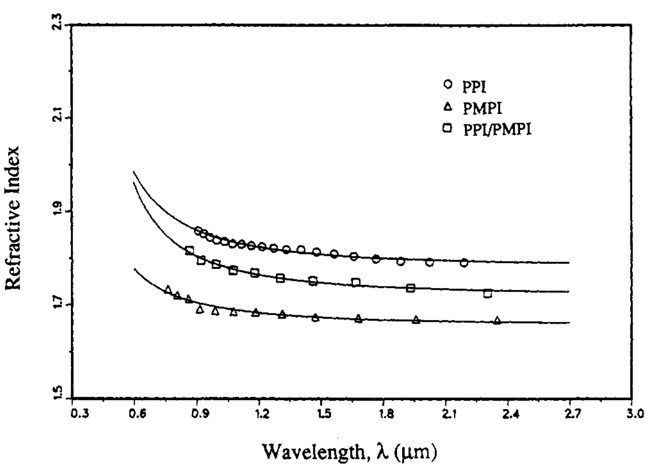

Figure 3. Refractive index dispersion data of PPI, PMPI, and the copolymer PPI/PMPI and their Sellmeier equation fit.

delocalization length and E_g is the optical bandgap. However, another contribution to the polarizability that may not be fully reflected in the above scaling law is the effects of polarizable heteroatoms, such as N, S, and O, whose lone pairs of electrons may not be part of the π-system of the conjugated polymer. In addition to the electronic and atom contributions to the polarizability α, orientation of the molecules could also be a factor; however, orientation polarizability is expected to be negligible in these isotropic materials. Even with these limitations, the optical bandgap E_g is a good, independent, approximate measure of the polarizability of a conjugated polymer.

Figure 2 shows the refractive index dispersion of several backbone variations in the polyimines (PPI, PBPI, PSPI, 1,5-PNI, and PBEPI). The solid lines through the data are the fits of Sellmeier equation as described previously. These five polyimines constitute the different polymer backbones without any side-group substitution and hence reflect the cases where effects of polarizability and electronic delocalization are expected to dominate the refractive index. Among the five backbone structures, 4,4′-biphenylene-, 1,5-naphthalene-, and 1,4-phenylene-linked polyimines which correspond to PBPI, 1,5-PNI, and PPI, respectively, have essentially identical refractive index in the 1.2–2.5-μm region. Far off-resonance at 2.5 μm, the numerical value of the refractive index of these three polymers is 1.79 as shown in Table 3. The similarity of the refractive indices of PPI, PBPI, and 1,5-PNI reflects the similarity of their π-electron delocalization as measured by optical bandgaps (E_g = 2.50–2.53 eV, Table 3). However, this does not necessarily mean similarity of the polarizability of the three conjugated polymers since their molar volumes differ by up to 33–40% (Table 3). The insersion of a *trans*-vinylene group between the phenylenes of the 4,4′-biphenylene in PBPI gives a polyimine, PSPI, with an increase in electronic delocalization as measured by the smaller optical bandgap of 2.38 eV. However, as shown in Figure 2, PSPI has a significantly smaller refractive index than PBPI; the refractive index of PSPI which is 1.69 at 2.5 μm represents a 0.10 decrease from that of PBPI. On the other hand, the refractive index of the 4,4′-biphenylene ether linked polymer, PBEPI, is significantly higher than that of PSPI but reduced relative to PBPI in spite of the break in conjugation in PBEPI. These results indicate the importance of polarizable heteroatoms in enhancing the refractive power of organic polymers. Thus, the reason PSPI has a significantly smaller refractive index compared to PPI is due to the replacement of the more polarizable imine (—CH=N—) linkage with the less polarizable vinylene (—CH=CH—) linkage and the increase in molar volume in going from PPI to PSPI. The present refractive index of the parent polyimine PPI is significantly larger than that of the structurally isoelectronic poly(*p*-phenylenevinylene) (PPV) which has a reported refractive index of 1.60 at 602 nm.[13] Conjugated aromatic polyimines in general can be expected to have higher refractive indices compared to their corresponding arylenevinylene polymers because of the greater polarizability of the nitrogen heteroatoms in the former polymers.

A side-group substituent is expected to influence the refractive index of a polymer primarily by its effects on molar volume and, depending on the side group's electron-withdrawing or -donating properties, secondarily by its polarizability and modulation of electronic delocalization in the polymer backbone. The simplest side-group substitution was the incorporation of a methyl group on one of the two phenylene rings of PPI, resulting in PMPI (Chart 1). The methyl substitution had no effect on the electronic delocalization since both PPI and PMPI have essentially identical optical bandgap (E_g = 2.49–2.50 eV). However, as shown in Figure 3, the refractive index of PMPI is reduced by 0.13 or about 7.3% throughout the wavelength range investigated. The reduction in the refractive index of PMPI relative to PPI is due entirely to the increase in molar volume by the presence of the methyl substitution.

Also shown in Figure 3 is the refractive index dispersion of a random copolymer PPI/PMPI which contains 52 mol % PPI as determined by ^{1}H NMR spectroscopy.[25a] The refractive index of the copolymer is the molar average of those of the component PPI and PMPI, indicating linearity of the refractive index with copolymer composition and similar to the copolymer composition dependence found in nonconjugated polymers such as polysiloxanes.[36] In contrast, we have found in studies of the nonlinear optical properties of PPI/PMPI copolymer that the copolymer

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(35) (a) Davies, P. L. *Trans. Faraday Soc.* **1952**, *48*, 789. (b) Flytzanis, C. In *Nonlinear Optical Properties of Organic Molecules And Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vol. 2, pp 121–135.

(36) Kohjiya, S.; Kazuyuki, M.; Yamashita, S.; Shibata, Y. *J. Mater. Sci.* **1990**, *25*, 3368.

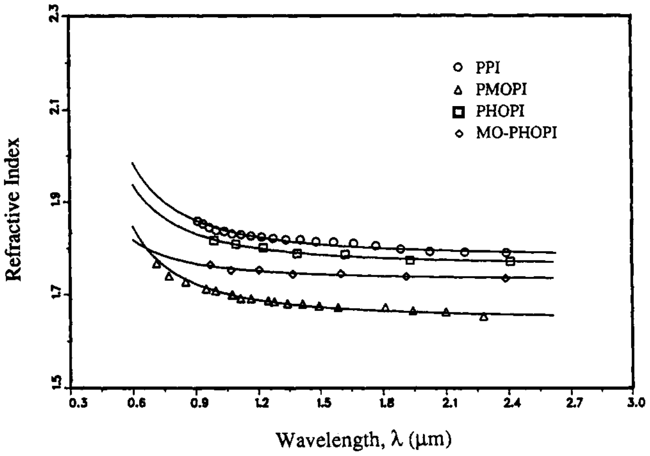

Figure 4. Refractive index dispersion data of PPI, PMOPI, PHOPI, and MO-PHOPI and their Sellmeier equation fit.

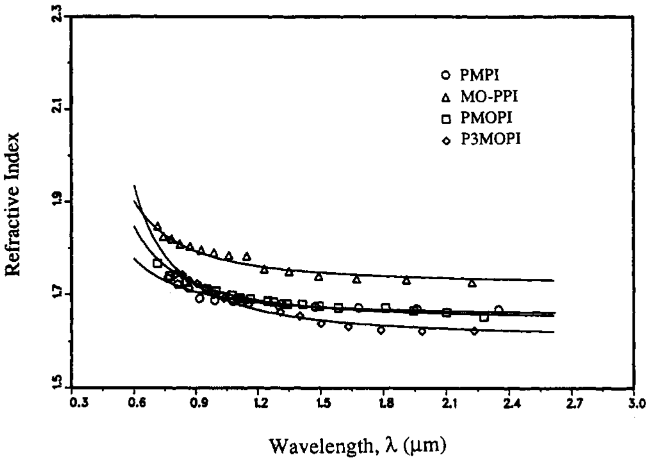

Figure 5. Refractive index dispersion data of MO-PPI, PMPI, PMOPI, and P3MOPI and their Sellmeier equation fit.

composition dependence of the third-order nonlinear optical susceptibility is not linear.[17b]

Effects of various combinations of electron donor side-group substitutents (OCH_3, OH) on the refractive index dispersion of several conjugated polyimines are shown in Figures 4 and 5. The solid lines in the figures are Sellmeier equation fits to the data. Compared to the refractive index of PPI, the dimethoxy side group in PMOPI results in 0.13–0.14 decrease of the refractive index in the 1.0–2.5-μm spectral range (Figure 4, Table 3). As shown in Figure 5, PMOPI has the same wavelength-dependent refractive index as the methyl-substituted PMPI. The identical values of the refractive indices of PMOPI and PMPI indicate that the dimethoxy groups results in a higher polarizability than the methyl group, and this is consistent with the much smaller optical bandgap in PMOPI than in PMPI (Table 3). However, the increased polarizability of PMOPI due to dimethoxy substitution is exactly compensated by an increase in molar volume compared to PMPI (Table 3). A comparison of methoxy substitution in MO-PPI to methyl substitution in PMPI shows that the refractive index of MO-PPI is significantly higher by 4–5% in the 1.0–2.5-μm range (Figure 5). Although methoxy group is slightly more bulky than methyl group and hence the molar volume of MO-PPI is slightly more than PMPI, the much larger polarizability of MO-PPI due to the methoxy group accounts for its higher refractive index. As the number of methoxy side groups added to the polymer repeat unit increases from one in MO-PPI to two in PMOPI the increase in molar volume is significantly more than the increase in polarizability, resulting in a smaller refractive index in PMOPI (Figure 5, Table 3). Addition of a third methoxy per repeat unit as in P3MOPI results in a further reduction of the refractive index as shown in Figure 5. The far off-resonance refractive index of P3MOPI at 2500 nm is 1.62 which is the smallest value among the 14 polyimines investigated and collected in Table 3. A good linear relationship between the off-resonant refractive index at 2500 nm ($n_{2500\ \mathrm{nm}}$) and the number of methoxy side group per repeat unit was found. This means that the off-resonant refractive index scales linearly with decreasing molar volume in these four polymers as verified in Figure 6. From the linear relationship of Figure 6 one can predict an off-resonance refractive index at 2500 nm to be 1.55 for the conjugated polyimine with 2,5-dimethoxy substitution on each phenylene ring, i.e., poly(2,5-dimethoxy-1,4-phenyleneimine), which is yet to be synthesized.

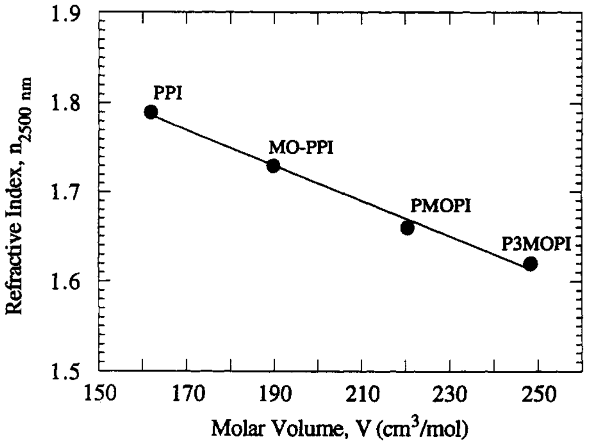

Figure 6. Refractive index ($n_{2500\ \mathrm{nm}}$) dependence on molar volume of methoxy-substituted polyimines.

Another interesting effect of the side group substitution on the refractive index of conjugated polyimines involves dihydroxy groups in PHOPI and MO-PHOPI whose refractive index dispersion are also shown in Figure 4. Compared to the refractive index of PPI, PHOPI and MO-PHOPI have refractive indices that are reduced by 1.1 and 2.8%, respectively. The high refractive index of PHOPI in spite of the dihydroxy substitution is due to the near balance between the increase of the refractive index by increase in polarizability and its decrease from increase in molar volume (Table 3). The polarizability of MO-PHOPI is about the same as PHOPI, as judged from their identical optical bandgap (E_g = 2.03–2.07 eV, Table 3), so that the smaller refractive index of MO-PHOPI (Figure 4, Table 3) is accounted for by the increase in molar volume by adding the methoxy group (Table 3). Additional effects of side group substitutions on the refractive index were observed in comparing PSMOPI to PSPI and 1,5-PMONI to 1,5-PNI (Table 3). In each case the refractive index is reduced by the dimethoxy substitution.

Chemical Group Contributions to Refractive Index. Chemical group contributions to the molar refraction of molecules have been successfully used to predict the refractive index of nonconjugated polymers for many years.[22] The predicted values agree with experimental data within 1%.[21,22] These formulations include the Lorentz and Lorenz, Gladstone and Dale, and Vogel models[22] and the current tabulated molar refraction values

Table 4. Group Contribution Prediction of the Refractive Index, the Experimental Refractive Indices, and the Abbe Number of Conjugated Polyimines

polymer	n_{LL}	n_{GD}	n_V	$n_{D(589\ nm)}$	$n_{F(486\ nm)}$	$n_{C(656\ nm)}$	ν_d
PPI	1.766	1.756	1.744	2.00	2.15	1.95	5.0
PMPI	1.738	1.725	1.705	1.78	1.86	1.76	7.8
PPI/PMPI	1.750	1.759	1.722	1.98	2.25	1.91	2.9
PMOPI	1.622	1.659	1.656	1.86	2.02	1.81	4.1
PHOPI	1.773	1.752	1.703	1.95	2.07	1.90	5.6
MO-PPI	1.712	1.706	1.694	1.91	2.04	1.87	5.4
P3MOPI	1.635	1.632	1.626	1.96	2.33	1.86	2.0
MO-PHOPI	1.716	1.703	1.730	1.82	1.88	1.80	10.3
PBPI	1.744	1.735	1.730	2.10	2.37	2.01	3.1
PSPI	1.756	1.742	1.716	1.83	1.95	1.79	5.2
PSMOPI	1.682	1.675	1.657	2.15	3.09	1.98	1.0
1,5-PNI	1.774	1.767	1.952	2.24	2.79	2.11	1.8
1,5-PMONI	1.688	1.687	1.838	1.92	2.04	1.88	5.8
PBEPI	1.721	1.716	1.713	1.88	1.96	1.85	8.0

of chemical groups are based on the refractive index at the sodium D line (n_D, $\lambda = 589$ nm). Shown in Table 4 are the Lorentz and Lorenz (LL), Gladstone and Dale (GD), and Vogel (V) model predictions of the refractive indices of the conjugated polyimines in Chart 1. Also shown in Table 4 is the n_D values of the polymers obtained by means of the Sellmeier equation parameters in Table 2. There is clearly a large deviation between the predicted and experimental n_D values, the deviations being in the range of 4–22% for the Lorentz and Lorenz model which is the best among the three models. The reasons for this failure of the chemical group contribution models in predicting the refractive index of conjugated polymers are also obvious. Unlike nonconjugated polymers which are transparent with negligible absorption at 589 nm, most conjugated polymers such as the present polyimines are highly absorbing at 589 nm. In principle then, the conventional chemical group contribution predictions based on n_D should not be applicable to π-conjugated polymers because of wavelength dispersion effects. The importance of the effects of wavelength dispersion is underlined by the fact that the n_D values predicted by group contributions (i.e., n_{LL}, n_{GD}, and n_V in Table 4) are closer to the off-resonant experimental refractive index data at 2500 nm than to n_D data. However, even the comparison of the refractive index at 2500 nm and the predicted values indicates that there is still a large discrepancy between the data and any of the models. Therefore, despite its past success in predicting the refractive index of nonconjugated polymers, the chemical group-contribution approach based on existing molar refraction values at 589 nm is unsatisfactory for practical use in predicting the refractive indices of conjugated polymers.

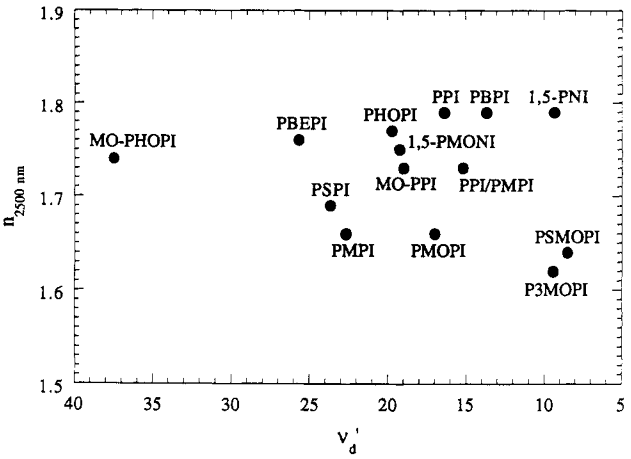

Figure 7. Refractive index and the modified Abbe number of conjugated polyimines.

Modified Abbe Number of Conjugated Polymers. With the Sellmeier equation and its parameters in Table 2, the refractive index at the hydrogen F line ($\lambda = 486$ nm) and C line ($\lambda = 656$ nm) were also calculated and are listed in Table 4. Compared to the refractive index at 2500 nm, there is a significant increase of the refractive index as the wavelength reaches 656, 589, and 486 nm. On the basis of the refractive indices at these specific wavelengths, the Abbe number ($\nu_d = (n_D - 1)/(n_F - n_C)$) is calculated to be in the range 1.0–10.3 (Table 4), which is too low for optical fiber applications.[2] However, it should be noted that the tabulations of refractive index at these wavelengths are of conventional interest and may not be appropriate since most conjugated polymers at regions such as the hydrogen F line ($\lambda = 486$ nm) and sodium D line ($\lambda = 589$ nm) have appreciable absorption. Therefore, the small Abbe numbers listed in Table 4 is simply a result of the resonance-enhanced and highly dispersive refractive index. Another definition of the figure of merit that accounts for the dispersive behavior of the refractive index of conjugated polymers in the transparent region is required. For example, the often measured refractive index at 1064 nm which is the Nd:YAG laser line, the relevant communication wavelength at 1319 nm,[37,38] and the off-resonant wavelength at 2500 nm appear to be suitable considerations for π-conjugated polymers. Referring to the refractive indices at 2500, 1319, and 1064 nm, a modified Abbe number is thus defined as

$$\nu_d' = \frac{n_{1319\ nm} - 1}{n_{1064\ nm} - n_{2500\ nm}} \tag{6}$$

The modified Abbe number defined in eq 6 and given in Table 3 ranges from 9 to 38 for these polymers. Figure 7 shows the refractive index at 2500 nm and the modified Abbe number of conjugated polyimines. Since the Abbe number ν_d' is a measure of the dispersion of refractive index, a high Abbe number ν_d' and consequently low chromatic aberration is preferred in optical devices.[2] Compared to the parent polyimine PPI, incorporating a polarizable aromatic unit along the polymer backbone such as in PBPI and 1,5-PNI results in a larger dispersion of refractive index and hence smaller ν_d' values. In contrast, the dihydroxy-substituted PHOPI and MO-PHOPI not only improve the polarizability and thereby increase the refractive index but also reduce the dispersion of refractive index as evidenced by their higher Abbe number. Contrary to the previous observation on the effects of structural modifications on the refractive index of nonconjugated polymers which indicates a concomitant decrease of Abbe number with increasing refractive index,[36] these data on the refractive index dispersion of conjugated polymers show that it is possible to reduce dispersion while maintaining a high refractive index.

Conclusions

A study of the structure–refractive index relationships in π-conjugated polymers has been facilitated by mea-

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(37) Stegeman, G. I.; Wright, E. M. *Opt. Quantum Electron.* **1990**, *22*, 95.

(38) Kim, D. Y.; Sundheimer, M.; Otomo, A.; Stegeman, G. I.; Winfried, H. G. H.; Mohlmann, G. R. *Appl. Phys. Lett.* **1993**, *63*, 290.

surements of the wavelength dispersion of the isotropic refractive index of a systematically designed series of π-conjugated polyimines shown in Chart 1. The refractive index dispersion data for the polyimines are reported in the convenient form of the Sellmeier equation which is found to describe the data well and allows interpolation of the data. The refractive index was found to vary with molecular structure in ways that can be accounted for by two competing molecular parameters: *polarizability*, which is related to the electronic delocalization as measured by optical bandgap; *molar volume*, which is accurately calculated for each polymer repeat unit. For example, methyl and methoxy substitutions on the parent conjugated polyimine backbone PPI result in identical refractive index in their transparent wavelength range because the methoxy group in the latter polymer (MO-PPI) decreases the index due to increase in molar volume but increases the index due to methoxy's positive contribution to the polarizability. The present refractive index data allowed us to test the applicability of the existing group contribution models for calculating the refractive indices of polymers to *π-conjugated polymers*. The large deviation between the predicted refractive index at 589 nm and the data suggests that current tabulated group contributions to molar refraction which are based on n_D *values of nonconjugated polymers* cannot be reliably used to predict the refractive indices of π-conjugated polymers. There is thus a need for new group molar refraction values suitable for predicting the refractive index of conjugated polymers which are of growing scientific interest as well as technological interest for applications in photonics and optoelectronics.

Acknowledgment. This work was supported by the New York State Science and Technology Foundation, Amoco Foundation, National Science Foundation, Center for Photoinduced Charge Transfer (Grant CHE-912-0001), and an Elon Huntington Hooker Fellowship to C.J.Y.