CAMBRIDGE

Cambridge University Press
978-1-107-40994-1 - Optical and Electrical Properties of Polymers: Symposium held November 26-28, 1990, Boston, Massachusetts, U.S.A.
Edited by John A. Emerson and John M. Torkelson
Excerpt
More information

PART I

Nonlinear Optical Effects in Polymers I

Doped Polymers as Third-Order Nonlinear-Optical Materials

Mark. G. Kuzyk
Dept. of Physics, Washington State University, Pullman, Washington

U. C. Paek
AT&T Bell Laboratories, Princeton, New Jersey

Carl W. Dirk
Dept. of Chemistry, University of Texas, El Paso, Texas

Mark P. Andrews
Dept. of Chemistry, McGill University, Montreal, Canada

1 Abstract

Recently, there has been much interest in doped polymeric materials owing to their suitability for optical device applications.[1] While most of this effort has been centered on poled polymers and their applications to electrooptics, doped polymers are beginning to emerge as a promising material class for all-optical device applications. In this contribution, we discuss the status of doped polymers as third-order optical materials. Particular attention is focused on those properties that make doped polymers attractive as device materials such as optical nonlinearity and loss and their suitability for nonlinear-optical fiber devices.

2 Introduction

All-optical devices share common material requirements.[2] The third-order optical susceptibility, $\chi^{(3)}$, must be large enough to affect a change in the propagation properties of an optical beam over the device's length, L, to perform, for example, a switching or logic function. The length of the device, however, must be short enough to allow a detectable level of light to pass through the device. In this chapter, we discuss those material properties that make doped polymers attractive in all-optical device applications.

The intensity dependent refractive index, Δn, depends on the intensity of the light in the nonlinear medium, I, and the cross sectional area of the beam, A, through the constant of proportionality, n_2:

$$\Delta n = n_2 \frac{I}{A}, \tag{1}$$

where n_2 is proportional to the third-order susceptibility, $\chi^{(3)}$. The phase, ϕ, of a light beam traveling through the nonlinear material will be affected by the refractive index change,

$$\Delta\phi = 2\pi n_2 \frac{I}{A}\frac{L}{\lambda}, \tag{2}$$

where λ is the wavelength of the light, and L, the length over which the nonlinearity acts on the beam. Most devices require a π phase shift to perform a function. The interaction length, L_π, that is needed to affect a π phase shift is given by:

$$L_\pi = \frac{A\lambda}{2n_2 I}. \tag{3}$$

Mat. Res. Soc. Symp. Proc. Vol. 214. ©1991 Materials Research Society

To maximize the nonlinear response of a device, then, one needs large intensities to be confined to small areas over long distances of highly nonlinear material. The amount of light absorbed or scattered by the material is given by αL, where α in the loss. To minimize optical loss, then, the device lengths must be made as short as possible with materials of low loss. A useful figure of merit is thus the nonlinearity-loss quotient, n_2/α.

In the next section, we discuss how the nonlinearity, n_2 (or equivalently, $\chi^{(3)}$), can be maximized by molecular engineering of the dopant to increase nonlinearity and solubility, and by using metal nanospheres for increasing local fields. After appropriate optimization of the material nonlinearity, the fabrication procedure for making low loss plastic nonlinear-optical fiber is discussed. The figure of merit for the polymer fibers is compared with that of glass fibers, which currently have the lowest losses and largest figures of merit.

3 Optical Nonlinearity

The third-order susceptibility of a doped polymer is additive over its substituents.[3][4] If γ^* is the dressed third-order susceptibility tensor, the bulk susceptibility tensor, $\chi^{(3)}_{ijkl}$, is related to the molecular values,

$$\chi^{(3)}_{ijkl} = N < \gamma^* >_{ijkl}, \tag{4}$$

where N is the number density of dopants and where the brackets <> denote the orientational average of the molecular susceptibility tensor.

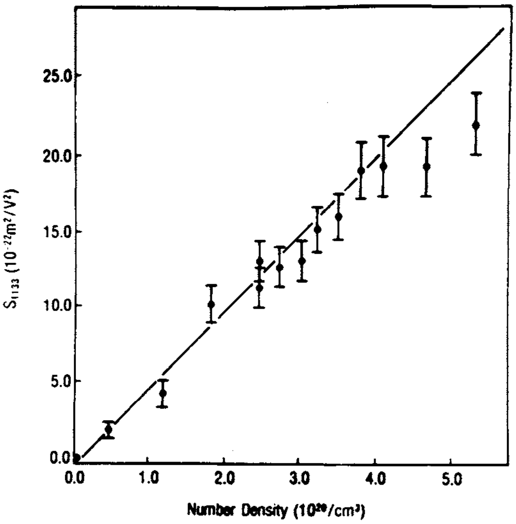

Figure 1. Number density dependence of the quadratic electrooptic coefficient, $s_{1133} \propto \chi^{(3)}$, for an azo dye.[4]

The applied electric field, $\vec{E}$, polarizes the material, so that the local field, $\vec{F}$, at the dopant sites is given by the sum of the applied field and the polarization field. These local fields can be calculated with local field models and are of the form:

$$F_i = L_{ii'} E_{i'}, \tag{5}$$

where $L_{ii'}$ is the local field tensor and where summation notation is implied. Because the third-order susceptibility tensor mixes four electric fields, the relationship between the dressed susceptibility, γ^*, and the vacuum susceptibility, γ, is:

$$\gamma^* = L_{ii'} L_{jj'} L_{kk'} L_{ll'} \gamma_{i'j'k'l'}. \tag{6}$$

To enhance the third-order susceptibility, then, one needs to increase the dopant concentration, increase the nonlinearity of the molecules and increase the local field factors. Figure 1. shows the linear dependence of the third-order susceptibility on dopant concentration. Below, we describe methods of molecular engineering to increase the dopant's third-order susceptibility and the use of quantum dots to increase the local fields.

3.1 Molecular Susceptibility

We use a two-level model to describe molecular properties that lead to a large third-order susceptibility. It must be pointed out, however, that a missing state analysis of several organic molecules shows that many states contribute to the third-order susceptibility.[5] Furthermore, molecular orbital calculations show that for certain materials such as octatetraene, at least three levels are needed to accurately determine the third-order susceptibility.[6][7] In the two-level model, the molecule is assumed to only have one dominant excited state. While it is not clear whether or not it is possible to have purely two-level systems, we show how a system that is nearly two-level was identified and measured to have a large third-order susceptibility.

Far off resonance, the two-level model for the molecular third-order susceptibility is of the form:

$$\gamma \propto \mu_{01}^2 \left(\mu_{01}^2 - (\Delta\mu)^2 \right), \tag{7}$$

where μ_{01} is the transition moment between the ground state and the dominant excited state, and where $\Delta\mu$ is the dipole moment difference $\Delta\mu = \mu_{11} - \mu_{00}$ between the excited state and the ground state. To maximize the third-order susceptibility, then, we must maximize each factor in Equation (7). The first factor is the square of the transition moment and is maximum for large transition moments. Because the second factor is the difference between the square of the transition moment and the square of the dipole moment difference, it is maximum when the dipole moment difference vanishes, $\Delta\mu = 0$. This condition holds for centrosymmetric molecules.

The maximum susceptibility in the two-level model, then, is attained in highly colored (large μ_{01}) centrosymmetric ($\Delta\mu = 0$) molecules. Perturbation calculations that take into account the interdependence of the transition moments and dipole moments confirm that the centrosymmetric limit is indeed maximum in the two-level system.[8] One class of such materials are the squarylium dyes.[9] Using quadratic electrooptic modulation (QUADEO), we have measured a series of molecules that include some highly polar molecules that are used for $\chi^{(2)}$ applications and the squarylium dye ISQ. The centrosymmetric squarylium dye is seen to have one of the largest QUADEO third-order susceptibilities.[4]

Figure 2. shows the molecular structures of the molecules while Table 1 summarizes the measured third-order susceptibilities.

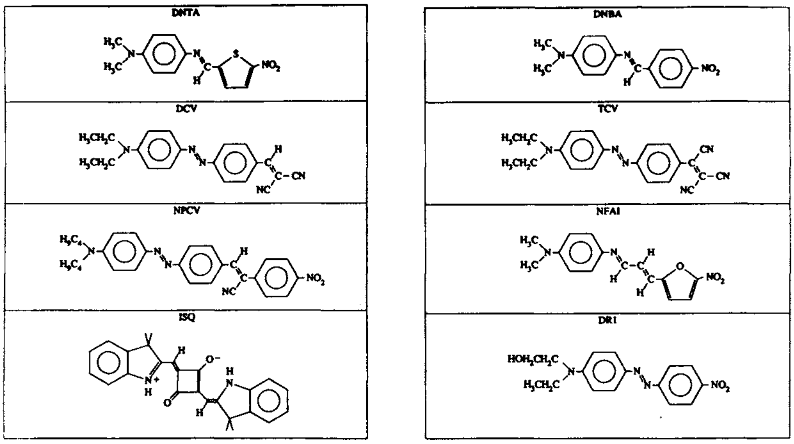

Figure 2. Molecular structures of third-order dye molecules.

Molecule	λ_{max} (nm)	S_{1133} $(10^{-22} m^2/V^2)$	$<\gamma^*_{zzzz}>$ $(10^{-34} esu)$	$\chi^{(3)}$ $(10^{-14} esu)$	N $(10^{20}/cm^3)$
DNBA	451	2.0 (±0.5)	2.3 (±0.6)	3.1 (±0.8)	1.37
DNTA	491	6.0 (±1.5)	3.4 (±0.8)	9.4 (±2.3)	2.76
NFAI	483	11.7 (±1.3)	6.6 (±0.7)	15.7 (±1.7)	2.40
DR1	491	12.9 (±2.0)	7.0 (±1.1)	17.0 (±2.6)	2.44
NPCV	515	6.7 (±1.5)	8.9 (±1.9)	10.5 (±2.3)	1.19
DCV	526	33.1 (±6.0)	41 (±8.1)†	60 (±12)†	1.48
TCV	598	30.2 (±6.0)	60 (±14)†	130 (±32)†	2.18
ISQ	658	10.7 (±1.5)	68 (±9.5)	12.9 (±1.8)	0.19

† The refractive index, n, was purposely overestimated owing to resonance enhancement, yielding values as upper limits of $<\gamma^*_{zzzz}>$ and $\chi^{(3)}$. Also, the orientational effects have not been taken into account so the dressed molecular third-order susceptibility could be systematically high by about 30% for the noncentrosymmetric molecules.

Table 1. Summary of third-order susceptibility measurements of γ of a series of dye molecules.[4]

3.2 Enhanced Local Fields

The local field at a molecule can be enhanced by doping the polymer with small metal spheres in the vicinity of the dye molecules. These spheres enhance the local fields by causing the applied field lines to bend in and concentrate at their surface. The electric field inside a dielectric sphere, E_{in}, is related to the applied field, $E_{applied}$, through the dielectric constant of the sphere, ϵ:

$$E_{in} = \frac{3E_{applied}}{\epsilon + 2}. \tag{8}$$

Near the plasma resonance of the metal, where $\epsilon \approx -2$, the field in the sphere is strongly enhanced.[10]

As discussed in the previous section, the dressed third-order susceptibility is proportional to the fourth power of the electric field and enhancements as large as 10^8 are possible.[10] To test these enhancement factors, we doped PMMA with small silver particles of $150\mu m$ diameter to concentrations of 0.045% by weight. Without local field enhancements, the third-order susceptibilities are expected to be below the detection limits of our quadratic electro-optic experiments.

In the experimental configuration, a Mach-Zehnder interferometer is used to measure the change of refractive index with applied electric field. The measured third-order susceptibility of our sample at $\lambda = 633$nm is $\chi^{(3)}_{1133} = 2.8(\pm 0.5) \times 10^{-14}$esu, an enhancement of five orders of magnitude over what is expected for silver without an enhanced local field. It is interesting to note that because the pump field in the QUADEO measurement is quasi-static, none of the pump field penetrates further into the sphere than the metal's skin depth, thus yielding mostly a surface nonlinear-optical response. While this susceptibility is small compared with that of molecule-doped polymers, large enhancements in a molecular dopant's third-order susceptibility may be achieved by either coating the surface of the metal spheres with the dyes or by depositing the dyes within the metal sphere boundary.

4 Nonlinear-Optical Polymer Fibers

In the previous section, methods for improving material nonlinearity are discussed. Here, we concentrate on the geometry of bulk structures that effectively use the nonlinearity of the materials. Optical fibers are convenient for confining light to small areas over long distances. This makes them ideal for nonlinear-optical device applications. An added benefit of fibers is that the optical losses tend to be smaller than that of the bulk material. The polymer fibers are drawn from a larger preform having the same relative dimensions as the final fiber as is discussed below.

The preform consists of the polymer poly(methyl methacrylate) (PMMA) in a rod form with a dye-doped core and neat PMMA cladding so that, after being drawn down to a thin fiber, light can be confined within the core and guided along the fiber axis. To support lightguiding within the core of the fiber, the index of refraction of the core must be slightly higher than that of the cladding. The relative index difference, Δ, is defined by,

$$\Delta = \frac{n_0 - n_1}{n_0} \tag{9}$$

where n_0 and n_1 are the index of refraction for the core and cladding, respectively.

The value of Δ for the plastic fiber we designed lies in the range of 0.35% - 0.4% to excite a single-mode for a core diameter of approximately $10\mu m$. The core index is raised relative to the cladding by doping it with a nonlinear squarylium dye imparting a large nonlinear effect on the guided mode. Typical doping levels of the squarylium dye were under 1% by weight. The core-to-clad ratio of the plastic preform is about 1 to 5 and the desired fiber core diameter can be obtained by controlling the total fiber diameter. A single-mode fiber core diameter, d for a given wavelength , λ, can be determined from the normalized

Cambridge University Press
978-1-107-40994-1 - Optical and Electrical Properties of Polymers: Symposium held November 26-28, 1990, Boston, Massachusetts, U.S.A.
Edited by John A. Emerson and John M. Torkelson
Excerpt
More information

frequency, V, that is defined by,

$$V = \frac{\pi d n_1 (2\Delta)^{1/2}}{\lambda} \tag{10}$$

To restrict guiding to only the lowest mode (HE_{11}) of the core, the V-value must be restricted to $V \leq 2.4$. For $\lambda = 1.55\mu m$ and $\Delta = 0.4\%$, the required core diameter for single mode guiding is about $8\mu m$. Note that the index of refraction of PMMA is approximately 1.48.

4.1 Polymer Fiber Drawing

Figure 3 shows a schematic of the polymer fiber drawing system, whose arrangement is similar to silica fiber drawing systems except for the lower furnace temperatures and shorter fiber drawing distances. For our polymer fiber apparatus, an electric heater furnace is used to heat the polymers up to 300^oC. Most polymer preform materials are softened within this temperature range. The heater has a gaussian-like temperature profile along its axis. Preform diameters typically range from 4mm to 10mm with lengths of about 200mm.

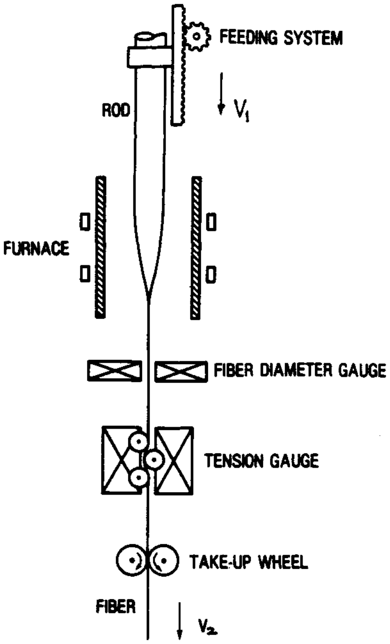

Figure 3.

The PMMA preform rod is fed through the electric heater that is set to a temperature between $100-150^o$C which is just above the polymer's glass transition temperature of $T_g \approx 100^oC$. The doped rod is peripherally heated and the viscosity of PMMA varies along the preform axis in accordance with the temperature profile of the heater. When the preform rod is stretched with pulling tension, the extensional deformation yields the "neck-down" region in the heater as shown in Figure 3. The shape of the neck-down depends on the draw parameters such as the heater temperature, T_h, preform diameter,

D_1, fiber diameter, D_2, feed speed, V_1, and fiber draw speed, V_2. The final fiber diameter is determined by the mass conservation relation of fiber draw, given by,

$$V_1 D_1^2 = V_2 D_2^2 \tag{11}$$

From the above equation, the fiber diameter, D_2 can be determined with any set of draw parameters.

4.2 Fiber Loss

There are several loss mechanisms in polymer fibers. They can be divided into two broad categories: scattering and absorption losses. Scattering losses arise from structures within the guiding region that are comparable to the wavelength of the propagating light, and, in the polymer fiber can be attributed to polymer inhomogeneity, dopant aggregation, scratches and other imperfections, and impurities. Absorption of light by stretch modes of the polymer chains, electronic excitation of dopants, and electronic excitations of impurities lead to absorption loss. The scattering losses can usually be minimized through material processing, while the material-intrinsic absorption losses are reduced by designing new materials with lower levels of absorption at wavelengths of interest.

In our ISQ/PMMA fibers, the total loss was measured at $\lambda = 1.3\mu m$ to be about 20dB/m. This loss is comparable to that of neat PMMA as measure by Kaino and coworkers.[11] The presence of the nonlinear dopants seems to have little effect on the loss. Because deuterated PMMA has been shown to have lower loss,[12] it is possible that further reductions in loss can also be achieved in our ISQ/PMMA fibers.

5 Discussion

It is interesting to compare the figure of merit of our doped polymer fibers with glass nonlinear-optical fibers. Because of the low loss of silica glasses, these materials have the best figures of merit despite their low nonlinearities. Table 2 summarizes the figures of merit of two glasses and the ISQ/PMMA fiber. While the figures of merit are comparable, it must be noted that the lower nonlinearities of the glass fibers require much longer interaction lengths to affect a π-phase shift than for the polymer fiber.

Material	$\lambda(\mu m)$	$\alpha(dB/m)$	$n_2(m^2/W)$	$n_2/\alpha(10^{-18}m^3/W \cdot dB)$
ISQ/PMMA	1.3	20	3.82×10^{-18}	0.2
Lead Glass$^+$	1.06	2.0	2.2×10^{-19}	0.1
Silica*	0.51	0.01	2.7×10^{-20}	2.7

*R. H. Stolen and C. Lin, Phys. Rev. A **17**, 1448 (1978).
+Newhouse et. al., Opt. Lett. **15**, 1185 (1990).

With present molecular dopant improvement efforts, it is reasonable to expect new molecules with susceptibilities that are two to four times larger than that of ISQ. Considering that solubilities can be increased from 1% to 5%, the bulk susceptibility can be increased by a factor of twenty. By deuterating the polymer, losses can be reduced by a factor of ten. With these two improvements, a 1 Watt beam of light in an $8\mu m$ diameter 0.3 meter fiber can induce a π phase change with a total loss of 0.6dB. This compares favorably with the silica fiber, which would require almost one kilometer of interaction length with a total loss of 9dB. Even without using enhanced local fields, these improvements result in at least a two-order of magnitude improvement over today's materials, making doped polymers attractive for third-order fiber-based devices.

6 Conclusion

Doped polymers, owing to their low loss and high nonlinearity, now have a reasonable figure of merit for all-optical device applications. With their processing flexibility, polymers can be made into long nonlinear-optical fibers with low loss and large intensity dependent phase shifts. New Polymer host materials and dopant dye molecules will no doubt lead to exciting improvements in the material's characteristics. With minimal material improvements, doped polymers will be useful for all-optical device applications.

Bibliography

1] see for example "New Materials for Nonlinear Optics," - American Chemical Society, ACS Symposium Series, vol xxx, S.R. Marder, J.E. Sohn, and G.D. Stucky, eds., ACS Washington, D.C., 1990/1991.

2] "Nonlinear Optical Effects in Organic Polymers," NATO ASI Series, Series E: Applied Sciences - vol 162, J. Messier, F. Kajzar, P. Prasad, and D. Ulrich, eds., Kluwer Academic Publishers, Dordrecht, 1989.

3] M. G. Kuzyk and C. W. Dirk, Appl. Phys. Lett **54**, 1628 (1989).

4] M. G. Kuzyk, C. W. Dirk, and J. E. Sohn, J. Opt. Soc. Am. B **5**, 842 (1990).

5] C. W. Dirk and M. G. Kuzyk, Phys Rev A **39**, 1219 (1989).

6] J. R. Heflin, K. Y. Wong, O. Zamani-Khamiri, and A. F. Garito, Phys. Rev. B **38**, 1573 (1988).

7] Z. G. Soos and S. Ramasesha, J. Chem. Phys. **90**, 1067 (1989

8] M. G. Kuzyk and C. W. Dirk, Phys. Rev. A **41**, 5098 (1990).

9] C. W. Dirk and M. G. Kuzyk, Chem. of Materials **2**, 5 (1990).

10] F. Hache, D. Ricard, and C. Flytzanis, J. Opt. Soc. Am. B. **3**, 1647 (1986).

11] T. Kaino, Japanese J. of Appl. Phys. **24**, 1661 (1985).

12] T. Kaino, K. Jinguji, and S. Nara, Appl. Phys. Lett. **42**, 567 (1983).