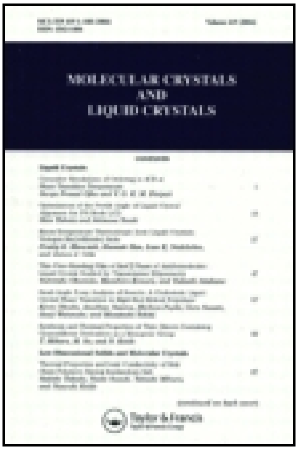

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# High-Temperature Electro-Optic Polymers

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To cite this article: J. W. Wu (1993): High-Temperature Electro-Optic Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 227:1, 61-69

To link to this article: http://dx.doi.org/10.1080/10587259308030961

*Mol. Cryst. Liq. Cryst.* 1993, Vol. 227, pp. 61–69
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Printed in the United States of America

# HIGH-TEMPERATURE ELECTRO-OPTIC POLYMERS

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## Abstract

The importance of electro-optic polymers in an application to a high-speed optical interconnection technology is discussed. A thermodynamically unstable nature of electric field poling is analyzed by introducing a rotational diffusion equation. The material requirements for useful electro-optic polymers are presented with regard to thermal stability and optical transparency. Polyimide guest-host system is discussed as an alternative to side-chain or epoxy polymers. Four different curing processes of guest-host polyimide systems are presented.

## 1. Introduction

The electro-optic (EO) effect is important as a second order nonlinear optical process realizable to a practical technology as well as in understanding the microscopic molecular electronic structures responsible for the nonlinear optical processes. EO effect, indeed, is already widely accepted as an important technology that can be employed in the optical interconnections alternative to the conventional electrical interconnections. Recent develpoments suggest that the communication bandwidth can be considerably increased through the EO polymer optical waveguide technology.[1][2][3]

The importance of these applications lead to an investigation of new nonlinear optical material classes. The second order nonlinear optical processes, as is well-known, are present only for a system lacking both the microscopic and the macroscopic inversion symmetry. This symmetry-breaking requirement restricts the available second order nonlinear optical materials to a limited number of material classes, that is, optical crystals and electric-field poled polymers. Two material classes, optical crystals and electric-field poled polymers, contrast in the stability and processibility. Optical crystals such as $LiNbO_3$ possess a thermodynamically stable structure, and give a moderate electro-optic coefficient. The bulk crystal shape, however, limits the compatibility with other technologically important materials, for example, semiconductor silicon chips. When an integrated optics incorporating the optical interconnection is envisioned, optical crystal remains as an isolated component. On the other hand, the electric-field poled polymers have a large compatibility with other electric materials, for example, photoresist coating and mask aligners. The ease of processibility such as spin-coating allows the polymer thin films integrable with the conventional semiconductor technology. The electric field poling, a macroscopic symmetry-breaking process, however, is thermodynamically unstable. Therefore the thermal and temporal stabilities of induced EO response are major issues in the application of nonlinear optical polymers to the integrated optics.

In Chapter 2, a microscopic mechanism for EO effect is reviewed, and the nature of electric-field poling is discussed in terms of orientational distribution function. Different classes of EO polymers are discussed in detail in Chapter 3. A recently developed polyimide guest-host system is introduced in Chapter 4, emphasizing the thermal stability of this new EO polymer. Chapter 5 concludes the paper.

## 2. Second Order Nonlinear Optical Susceptibility

First we look at the microscopic polarizabilities of molecular systems. The molecular polarizability can be obtained through a quantum mechanical perturbation method. When an external optical electric field is incident on a molecule, it perturbs the electronic wave function of the molecule resulting in the nonvanishing expectation value of the induced electric dipole moment. The induced electric dipole moment is expanded in terms of the optical electric field to give the linear and nonlinear polarizabilities. In this way the molecular polarizability is related to the transition matrices of the electronic states of the molecule. In the electric dipolar (E1) approximation, for example, the second rank tensorial linear polarizability $\alpha_{ij}$ is given as following.

$$\alpha_{ij}(-\omega;\omega) = \frac{e^2}{\hbar} S_T \sum_n < g \mid x_i \mid n >< n \mid x_j \mid g > \frac{1}{\omega_{ng} - \omega} \tag{1}$$

where $S_T$ is total symmetrization operator for the frequencies. Since the $x$ operator is odd under the parity operation and the linear polarizability $\alpha_{ij}$ is given as a sum of products of two transition moments, it's easy to see from the dipole selection rule that $\alpha_{ij}$ is always nonvanishing, regardless of the symmetry property of the molecular structure.

When the induced electric dipole moment is expanded one order higher than the linear polarizability, it is possible to expand in two different ways. One is to expand in the magnetic field, and the other is to expand in the electric field. In the magnetic dipolar (M1) approximation, the molecular polarizability is of the third rank tensor, and is related to the optical activity. In the electric dipolar (E1) approximation, the induced dipole moment of a molecule can be expanded up to the second order to give the molecular hyperpolarizability, $\beta_{ijk}$.[4]

$$\begin{aligned}&\beta_{ijk}(-\omega_1-\omega_2;\omega_1,\omega_2)\\&=\frac{e^3}{4\hbar^2}S_T\sum_{m,n}<g\mid x_i\mid m><m\mid x_j\mid n><n\mid x_k\mid g>\\&\times\frac{1}{(\omega_{mg}-\omega_1-\omega_2)(\omega_{ng}-\omega_2)}\end{aligned}\tag{2}$$

From Eq.(2) we find that the numerators of $\beta_{ijk}$ are given as a sum of products of three transition moments. According to the quantum mechanical dipole selection rule, when the parity is a good quantum number of the system, a product of odd number of transition moments vanishes identically. Therefore, we find that $\beta_{ijk}$ will be absent in a centrosymmetric molecular structure. But for a molecular structure without the inversion or the reflection symmetry the parity is not a good quantum number, hence, the value of $\beta_{ijk}$ will be nonvanishing in general.

The macroscopic nonlinear susceptibility $\chi^{(2)}_{\alpha\beta\gamma}$ can be found by considering the induced dipole moment $p_i^{\omega_1+\omega_2}$ and summing over the molecules.[5]

$$p_i^{\omega_1+\omega_2}=\beta_{ijk}(-\omega_1-\omega_2;\omega_1,\omega_2)E_j^{\omega_1}E_k^{\omega_2}\tag{3}$$

In the case of EO effect, one of the electric field is dc, and the other is an optical field. The EO induced molecular polarization, then, is simply given as

$$p_i^{\omega}=\beta_{ijk}(-\omega;\omega,0)E_j^{\omega}E_k^0\,.\tag{4}$$

To simplify the discussion, we assume that the only nonvanishing component of $\beta_{ijk}$ is $\beta_{333}$. In this case the EO induced molecular polarization is along the 3-axis of the molecule:

$$p_3^{\omega}=\beta_{333}(-\omega;\omega,0)E_3^{\omega}E_3^0\tag{5}$$

The macroscopic polarization along the $z$-axis is

$$\begin{aligned}P_z^{\omega}&=N\int p_3^{\omega}\cos(3,z)f(\Omega)d\Omega\\&=N\int\beta_{333}(-\omega;\omega,0)\cos^3(3,z)f(\Omega)d\Omega E_z^{\omega}E_z^0\end{aligned}\tag{6}$$

Another macroscopic polarization along the $x$-axis can be obtained by considering the external dc field along the $z$ direction and the external optical field along the $x$ direction.

$$\begin{aligned}P_x^{\omega}&=N\int p_3^{\omega}\cos(3,x)f(\Omega)d\Omega\\&=N\int\beta_{333}(-\omega;\omega,0)\cos^2(3,x)\cos(3,z)f(\Omega)d\Omega E_x^{\omega}E_z^0\end{aligned}\tag{7}$$

From the above relations we obtain the following relation for the macroscopic EO susceptibilities:

$$\chi^{(2)}_{zzz}(-\omega;\omega,0) = N\int \beta_{333}(-\omega;\omega,0)\cos^3(3,z)f(\Omega)d\Omega \tag{8}$$

$$\chi^{(2)}_{xxz}(-\omega;\omega,0) = N\int \beta_{333}(-\omega;\omega,0)\cos^2(3,x)\cos(3,z)f(\Omega)d\Omega \tag{9}$$

The statistical orientational distribution function $f(\Omega)$ follows the Mawell-Boltzmann distribution,

$$f(\Omega) \propto \exp\left(-U/kT\right). \tag{10}$$

The dipolar interaction energy of the polarizable dipoles with an electric field is simply given by [6]

$$\begin{aligned} U &= -\vec{\mu}\cdot\vec{E} - \frac{1}{2}\vec{p}\cdot\vec{E} \\ &= \text{const} - xkT\cos\theta - ykT\cos^2\theta\,. \end{aligned} \tag{11}$$

where the dimensionless parameters important in determining the distribution are defined as

$$x = \frac{\mu E}{kT},\; y = \frac{(\alpha_{\|}-\alpha_{\perp})E^2}{2kT}\,. \tag{12}$$

For second-order materials, where a noncentrosymmetric structure is required at both the microscopic molecular and global macroscopic levels, the interaction of the permanent dipole is dominant over the interaction of the induced dipole moments. Therefore, it is a good approximation to assume that $y \ll x$. With this approximation, the statistical distribution $f(\Omega)$ is

$$f(\Omega) = f(\theta) \propto \exp\left(x\cos\theta\right). \tag{13}$$

When the normalization is taken into account,

$$f(\theta) = \sum_{n=0}^{\infty}\frac{2n+1}{2}\frac{i_n(x)}{i_0(x)}P_n(\cos\theta) \tag{14}$$

where $i_n(x)$ are the spherical modified Bessel function, and $P_n(\cos\theta)$ are the Legendre polynomials.

After electric field poling, the statistical orientational distribution undergoes a rotational diffusion. The time-dependent diffusion process is described by a diffusion equation obtained through combination of Fick's law and the continuity equation.[5][7]

$$\frac{1}{D}\frac{\partial f(\theta,t)}{\partial t} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left\{(\sin\theta)\left[\frac{\partial}{\partial\theta}f(\theta,t) + \frac{1}{kT}\frac{\partial U}{\partial\theta}f(\theta,t)\right]\right\} \tag{15}$$

The transient behavior of orientational distribution function $f(\theta,t)$ can be described by introducing a time-dependent coefficient in the expansion of Eq.(14).

$$f(\theta,t) = \sum_{n=0}^{\infty} c_n(t)\frac{2n+1}{2}\frac{i_n(x)}{i_0(x)}P_n(\cos\theta) \tag{16}$$

Substitution of Eq.(16) into the rotational diffusion equation Eq.(15) gives the temporal behavior of on-rise and decay of EO response when the poling electric field is turned on and off. It is found that there are at least more than one time constant involved in the on and off processes. It is important to note that the EO response of an electric-field poled poly,er is in a thermodynamic nonequilibrium.

## 3. Electro-Optic Polymers

In the application of electro-optic polymers to an optical interconnection technology, there are certain material requirements to be satisfied. The semiconductor chip process, for example, involves a short excursion to a high temperature up to 300°C as well as a photoresist curing including ultraviolet exposure. The thermodynamically unstable, poled EO response should be able to survive all the material process steps for it to be compatible with silicon technology. In these regards, there are three stability issues. One is the stability of the order parameter of orientational distribution of molecular dipoles. The rotational diffusion constant appearing in Eq.(15) must be large enough, or the rotational decay time must be long enough so that there is no appreciable decrease of EO coefficient during and after the material processes. Another issue is the stability of chromophores doped inside the polymer matrix. Usually the $\pi$-conjugation giving a large electron correlation effect responsible for a large electronic nonlinearity [8] has a poor thermal stability. A thermal decomposition of chromophore through a $\pi$-conjugation breaking is a serious problem when a high temperature process is involved. The last issue might be a thermal stability of the host polymer matrix itself. The well-known methacrylate type polymer, for instance, has a relatively low glass transition temperature around 100°C. Above the glass transition temperature, the low viscosity of the polymer allows the electric-field poling of the molecular dipoles. The presence of a low glass transition temperature, however, offers a difficulty when the induced alignment of dipoles needs to be maintained. Glass transition can be viewed as a second order thermodynamic phase transition[9], where the free volume of the polymer undergoes a continuous change. Usually an alipahtic structure of polymer backbone possesses a large free volume, resulting in a low glass transition temperature. This consideration leads to the investigation of a new host polymer with small free volumes.

There are two well known types of polymers that have been employed as host polymers in EO polymers: thermoplastics and thermosets. Thermoplastic polymers, in general, possess a glass transition temperature $T_g$ associated with a thermodynamic second order phase transition. As discussed above, the thermal stability of the EO polymer is limited by the inherent $T_g$. To increase the thermal stability of acrylate-based thermoplastic polymer systems, side-chain attachment[10] and main-chain incorporation of the nonlinear optical moiety have been used to achieve maximum stability and doping concentrations. Thermosets, on the other hand, are prepared through a curing process. In the pre-cured form these polymers are highly processible by spin-coating, spray-coating or casting in molds. Typical cure processes involve either thermocycling or uv illumination. Improvements in electric-field poled polymer thermal stability via cross-linking have been demonstrated in both thermocycled[11] and uv illuminated[12] systems. With side-chain polymers and epoxy-type cross-linking systems, electro-optic thermal stability at temperatures near 100°C has been reported. However, acrylate and epoxy type polymeric materials appear to fundamentally limit the thermal stability to tempeatures near 200°C due to chemical decomposition of the base material. For generally useful devices, higher-temperature based material stability is required.

In a typical application of EO polymer to optical waveguides, the optical phase of laser light is modulated through the electrodes in the active region of polymeric waveguides. Since the accumulated phase shift is linearly proportional to the distance the light has travelled, the optical loss in the waveguide should be minimized in the active switching region. The optical losses are either from the dye chromophores or from the polymer backbone itself. Absorption loss of molecules can be reduced by operating the system in the off-resonance regime, while the scattering loss from the domain formations of polymer matrix is hard to get rid of. It is found that a cross-linking process usually induces a large scattering loss.

## 4. Guest-Host Polyimide Systems

Polyimide is a well-known class of polymer that is used in the semiconductor industry as a thin film dielectric insulator. Representive material properties are shown in Table 1. It is thermally stable to 400°C, has a low thermal expansion coefficient, and a high electric resistivity, and is already in a wide use in semiphotonics, the application of polyimides as passive optical waveguide materials for optical interconnects is already being heavily pursued. The fabrication of micro-size structures in polyimide films on top of silicon-based devices, for example, has recently been demonstrated.[13]

| | |
|---|---|
| Density | 1.38 gm/cm$^3$ |
| Coefficient of Thermal Expansion | 35 × $10^{-6}$cm/cm-°C |
| Dielectric Strength | 300 V/$\mu$m |
| Dielectric Constant (1 MHz) | 3.5 |
| Dissipation Factor (1 MHz) | 0.002 |
| Volume Resistivity | 1 × $10^{15}$ Ohm-cm |
| Tensile Modulus | 300 kg/mm$^2$ |
| Maximum Service Temperature | 400°C |

Table 1. Representive Properties of Polyimides [15]

Polyimides are available which have high optical transparency, a coefficient of thermal expansion comparable to silicon wafers, and refined micro-electronics process compatibilities.[14][15] Available as polyamic acid solutions, which are the initial condensation products of the reaction between a dianhydride and a diamine in aprotic solvnets such as N-methyl pyrolidinone (NMP), these resins are easily coated as thin films using a variety of techniques (e.g., spin and spray coating).

In the application of polyimides as host matrix for electro-optic polymers, a guest-host system is already well-developed. Guest-host polyimide systems include at least four differnt types when classified based on the curing processes: (1) electric-field poling through a thermal imidization,[16] (2) electric-field poling through the densification,[17] (3) chemical imidization after electric-field poling,[18] (4) thermoplasticity poling after curing.[19]

Polyamic acid, a precurser form of diamine and dianhydride, can be imidized thermally at around 150 to 160°C. The imide ring is formed through a dehydration process, and the achieved polyimide linkage gives a rigid planar structure to the cured film. A mixture of nonlinear optical chromophore and polyamic acid solution is spin-coated as a thin film on a substrate with coplanar elelctrodes. After a soft baking, the film can be electric-field poled throughout the thermal imidization. The EO response is found to be stable after many hours of thermal aging at 150°C. A higher thermal stability is shown to be obtained when the densification process occuring at 350°C and above, is employed for curing. For example, a thermal aging test at 200°C for 80 hours shows that there is no virtual decay of EO signal aside from an initial decrease of EO response around 30%. Densfication significantly enhances thermal stability, which is from the packing of polyimide linkages related to a further decrease of free volumes. Certain stilbene or azo dye type nonlinear optical molecules such as disperse red or dimethylamino-nitro stilbenes have a limited thermal stability itself owing to the charge correlated $\pi$ conjugation bonds. In order to overcome this chemical decomposition problem, a room temperature chemical imidization can be employed. After the film is electric-field poled at a relatively low temperature 150°C for half an hour, the imidization can be completed by a room temperature dehyration process, that is, by immersing in a dehydrant. Thermal aging test shows that this completion of imidization at room temperature greatly enhances thermal stability when compared with the sample not chemically dehydrated. Eventhough the imidization is a thermal setting process, the aliphatic polyimides exhibit a thermoplastic behavior. This suggests that a cured film of mixture of nonlinear optical chromophore and polyimide can be poled above a glass transition temperature at a parallel plate structure. Samples prepared in this way possess a dielectric reponse superior to an acrylate type polymer. A thermal stability up to 150°C has been demonstrated in a disperse-red-1 and PIQ2200 polyimide system.

## 5. Conclusion

In summary, electro-optic polymers are compared with optical crystals in the application of electro-optic materials for optical interconnects. A thermodynamically unstable nature of electric field poling is discussed with relation to material requirements for a useful electro-optic polymer. Polyimide guest-host systems possessing high thermal stability and low optical loss are presented as an alternative to side-chain or epoxy polymers. It is shown that there are four different curing processes for guest-host polyimide system.

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