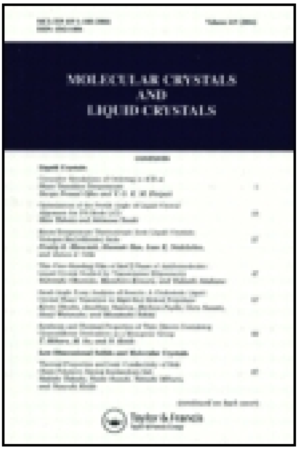

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Development of Polymeric Nonlinear Optical Material

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DEVELOPMENT OF POLYMERIC NONLINEAR OPTICAL MATERIALS

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Abstract The molecular structural characteristics which give rise to large optical nonlinearities have been delineated. This has been accomplished by several key steps and has led to the development of a structural algorithm for the design of β molecules with high susceptibilities. High activity molecular units have been covalently attached to form polymers which can contain up to 100% of the NLO moiety, and the resulting molecular optical properties have been characterized. The second order molecular susceptibility was found to be undiminished by properly designed covalent bonding to form a polymer, and spectral characteristics were found to closely follow that of the NLO unit.

INTRODUCTION

The need to increase the speed, information content, and the amount of multiplexing delivered via lightwaves for communications, computing, and dedicated information systems require the development of fast, high activity nonlinear optical (NLO) materials that are easily processed. It is obvious that to meet these requirements, various aspects of existing lightwave technology must be further developed. Improvements in lasers have satisfied many of the light source requirements for these needs, but not all. For example, direct modulation of the laser can take the technology only so far since deleterious side effects, such as chirping, occur when this method is used[1,2]. Therefore, nonlinear optical (NLO) devices are desirable to process the laser light so that systems capable of even faster, higher information content communications or computation can be developed.

Currently available NLO inorganic crystalline materials are not adequate for the desired device characteristics particularly when coupled with semiconductor lasers. The intrinsic properties of organic NLO materials offer significant advantages in both the magnitude and the speed of NLO effects over a broad range of wavelengths. Although organic crystalline materials eliminate some major inadequacies of inorganic crystalline materials, fabrication requirements for NLO devices for the semiconductor industry make single crystal technology unacceptable for most device designs.

We are engaged in a program to develop NLO polymers. Such materials possess not only the enhanced magnitude and speed of organic materials, but also the attractive advantages of polymer processing. These materials are projected to be wholly adequate for NLO device development. Further, these materials are the only potential materials which are projected to meet device requirements for the entire range of communications, computing, and dedicated information systems. In this paper, these design concepts will be highlighted in an attempt to define an industrial processing approach to this material problem.

MOLECULAR DESIGN OF NLO MOLECULES

Nonlinear optics is primarily concerned with response of a dielectric material to a strong electromagnetic field. The material response is formally represented by a dielectric constitutive equation of the following form:

$$P_i = P_{o,i} + \chi^{(1)}_{ij} E_j + \chi^{(2)}_{ijk} E_j E_k + \chi^{(3)}_{ijkl} E_j E_k E_l + \ldots$$

where P_i is the i-th component of the polarization, $P_{o,i}$ the permanent polarization, $\chi^{(1)}$ the linear electronic susceptibility, and $\chi^{(2)}$ and $\chi^{(3)}$ the second and third order susceptibilities. In Equation I, summation over repeated indices is assumed. In this paper, we are primarily concerned with second order NLO materials, i.e., materials exhibiting a large $\chi^{(2)}$. Applications of second order materials may be a linear electro-optic modulator, such as a directional coupler in optical communication, a frequency doubler using second harmonic generation, or a parametric oscillator.

The macroscopic NLO behavior of organic NLO materials originates from the polarization response of molecular electrons. Similar to Equation I, the molecular polarization behavior can formally be expressed as[3]

$$\mu_i = \mu_{o,i} + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \ldots$$

where μ is the dipole moment of the molecule in electrical fields, $\mu_{o,i}$, the permanent dipole moment, α, the polarizability, β and γ the second and third order hyperpolarizabilities, respectively. When molecules are immobile in the applied electrical or optical field (which is the case with most solid samples), $\chi^{(2)}$ results directly from the molecular hyperpolarizability, β. Optimization of $\chi^{(2)}$ of NLO polymers, therefore, can begin from optimizing the molecular structure to increase β.

Because of their ordered tensorial character, both $\chi^{(2)}$ and β automatically vanish in a centrosymmetric material system. It then follows that for a material to display second order NLO behavior, it must contain not only *noncentrosymmetric* NLO moieties at the molecular level, but also these must be spatially arranged in a noncentrosymmetric manner macroscopically. Thus, the development of NLO polymeric materials requires: (1) the design of noncentric NLO organic moieties with large molecular susceptibilities (e.g. β for $\chi^{(2)}$), (2) the incorporation of these moieties into tractable, optically clear polymers, and (3) the fabrication of polymers to control orientation and symmetry of the final material (e.g. a *noncentric oriented structure is required for* $\chi^{(2)}$ materials). Therefore, design of noncentric high β molecules is an essential but not wholly sufficient for the development of $\chi^{(2)}$ NLO polymers.

An absolute measurement technique for β is DC second harmonic generation (DCSHG). The DCSHG technique[4], however, requires a complicated set of instruments and relatively high concentrations of NLO molecules in solution. In view of the large number of samples that were generated and a need to rapidly feed back the information to the synthetic chemists, an alternative experimental technique called "solvatochromism" was used for this study[5]. The method is based on the experimental observation that the light absorption frequency of dipolar molecules is dependent on the solvent polarity and the solvent dependent frequency shift originates from the same molecular electronic factors as the molecular second hyperpolarizability. Furthermore, the solvatochromism experiments are relatively easy laboratory experiments and data can be quickly analyzed and readily fed back for the next research iteration. This technique permits the generation of an extensive data base of β for various organic molecules.

This technique for determining the molecular susceptibility of organic NLO molecules has been treated in detail elsewhere[6]. However, various generalities as to what functional groups and structural criteria play important roles in the molecular NLO activity can be easily identified by this method. These features are really quite obvious in terms of constructing molecular units which, in an intense optical field, produce a large nonlinear induced dipole moment.

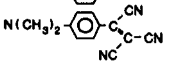
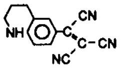
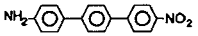
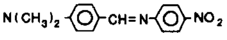
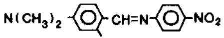
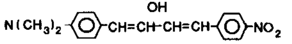
Conjugation, planarity, and length all play a direct role in determining the magnitude of the induced dipole moment. An asymmetric electronic environment is achieved through the use of electron donating (amines, methyl, etc.) and accepting (halogens, nitro, cyano, etc.) groups. For a linear molecule, it is apparent that placing these units at opposing ends of a conjugated molecule will impart a directionality to the induced dipole moment and a dependence of the induced dipole moment upon even order powers (e.g. those requiring a noncentrosymmetric habit) of the electric field. Examples of the effects of structure on the magnitude of β as determined by the solvatochromism method is given in Table 1.

The ability to gain molecular control of β through synthesis is clearly outlined in Table 1 where the effects of changing group, length, and planarity are elucidated. The control material, para-nitroaniline (PNA), has a measured β of 5.7. Replacing the nitro group with a more effective electron attractor in Compound 2 increases the β to 21.4. While an effective donator, the dimethylamino group in this compound is not quite coplanar with the rest of the molecule; thus, maximum conjugation cannot be achieved. Forcing the nitrogen into coplanarity through covalent bonding to the benzene ring (Compound 3) results in an effective doubling of β to 41.8. The effect of increasing the conjugation length on β is clearly seen from Compounds 1, 4, and 5. An order of magnitude increase in β can be realized in going from one benzene ring (PNA) to three. Planarity also plays an important role. The azomethine linkage (Compound 6) is not planar and will disrupt conjugation in the molecule shown. However, incorporation of an ortho hydroxyl group (Compound 7) forces the molecule into planarity through hydrogen bonding resulting in a threefold increase in β.

A combination of all these effects into a single molecule produces a material whose β is almost 20 times the control.

TABLE 1. Molecular Structural Control of β

Molecular Structural Control of β

Structure	**β at 1.9 μm (x 10^{-30}esu)**	**Comment**
	5.7	Standard
	21.4	Group
	41.8	Group
	20.1	Length
	50.7	Length
	23.4	Planarity
	61.6	Planarity
	111.2	All

A. Buckley et al. Polymeric Materials Science & Engineering Proceedings of the ACS Division of Polymeric Materials: Science & Engineering Vol 54, pg 502. 1986

NLO SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

Certain design criteria for low molecular weight organics with exceptionally high molecular hyperpolarizability have been established. A number of monomer molecules have been prepared in accordance with these criteria and have been shown to have the same hyperpolarizabilities as the small molecule models.

While some of these compounds have been grown as single crystals with a proper crystal symmetry for NLO application, the single crystal approach for NLO materials suffers from inherent difficulties. Most importantly, the resulting symmetry and orientation of molecular units packed within a unit cell cannot be controlled by chemical synthesis or the application of external forces. In addition, formation of the requisite noncentrosymmetric symmetry for $\chi^{(2)}$ materials is generally opposed by the highly dipolar character of these molecules.

Guest/host materials in which the small molecule models are dissolved in a polymeric matrix have been extensively studied at Hoechst Celanese and possess many attractive properties. However, guest/host materials suffer from limited solubility of the active species in a polymer host which lowers the achievable level of the nonlinear optical properties. Other problems such as phase separation, nonuniformity in the dispersion and migration of the active species are also prevalent.

Many of these difficulties are overcome when the NLO active species are chemically attached to polymer chains. Polymers allow for high concentration of the active moiety and can be manipulated by various processing techniques into different sizes, shapes, and degree of orientation. Once frozen below Tg, their long relaxation times can be utilized to maintain the desired structure at ambient temperature for an indefinite period of time.

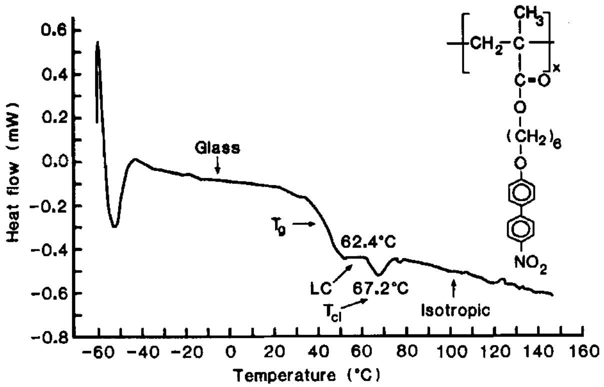
To obtain a response from the second order NLO coefficient β, alignment and the extent of noncentrosymmetry of the active units in the polymer are critically important for maximizing the NLO response of the material. Unoriented polymers are by definition centrosymmetric and have no $\chi^{(2)}$ properties, whereas orienting the dipoles of high β moieties in the same direction produces high $\chi^{(2)}$ values. Therefore, the ability to control the orientation and symmetry of a polymeric material is critically important to its final NLO response.

Many of the structural requirements for NLO active organic molecules are shared by liquid crystalline mesogens. Therefore, considerable effort has been spent to create NLO polymers in which the NLO moiety has a shape similar to what is expected to induce a liquid crystalline phase. By achieving liquid crystallinity, oriented $\chi^{(3)}$ materials may be fabricated by typical polymer techniques. Further, electrical poling of oriented liquid crystalline polymers will produce an enhanced degree of noncentric alignment for $\chi^{(2)}$ applications.

Some of the materials currently under investigation are side chain liquid crystal polymers. A DSC trace of a typical NLO active side chain liquid crystalline polymer is illustrated in Figure 2. The polymer chains are typically composed of three parts: backbone, side chain spacer groups and NLO active mesogenic units[7-13]. Intermolecular interaction between the mesogens and, to a lesser extent, between the spacer groups results in mesophase formation in melts of these polymers. The function of the spacer group is to decouple the side chain motion from that of the backbone, otherwise the latter will effect the stability of the liquid crystal phase. By appropriate manipulation of the backbone, spacer and NLO group, a variety of mesophases can be realized in these polymers. Nematic, cholesteric, smectic A and smectic C mesophases have been observed in various liquid crystal polymers[14].

Smectic phases are layered structures consisting of "layers" of molecules that can exhibit both orientational order and translational order between the smectic layers. Many different types of smectics exist displaying varying degrees of order both within an individual smectic layer and between layers. Unoriented smectics show a texture in which the layers are aligned within each domain on a micron or submicron scale. However, in the naturally occurring texture, the individual domains are randomly oriented with respect to one another. Upon application of external forces, smectics are able to form large monodomains in which very high orientational order approaching that of a single crystal is achieved (i.e. orientational order parameters exceeding 0.85). With domain alignment, light scattering from defects is eliminated and the sample becomes optically transparent. The transition from a highly scattering polydomain state to a transparent monodomain state has been used as a method for optical storage[15].

FIGURE 2. DSC Trace of NLO Active Liquid Crystal Polymer



In principal, liquid crystalline polymers can display all of the phases observed for small molecule liquid crystals. In addition, as polymers, these materials possess a glass transition temperature so that the molecular order for a given phase may be frozen for use over a wide range of temperatures. For NLO applications, side chain polymers are favored because of their high degree of order in the LC phase. Furthermore, utilizing the slow relaxation characteristics of the glassy state in polymers, we may generate three different NLO samples from these polymers: (1) unoriented $\chi^{(3)}$ material, (2) oriented $\chi^{(3)}$ material by cooling an aligned smectic A structure, (3) oriented $\chi^{(2)}$ material by poling the sample under a high electrical field.

The first series of side chain polymers investigated are shown in Figure 3. The mesogen/NLO unit is 4-hydroxy-4'-nitrobiphenyl and the spacer lengths are varied as shown. Although this particular moiety has a β that is only 80% the value of MNA, it was chosen because of its relative ease of synthesis through common synthetic methods. This allows preparation of sufficient quantities of material for fabrication, poling, and device research. These "first generation" polymers provide an initial data base by which future higher activity materials will be investigated.

The synthesis of these materials is outlined in Figures 4 and 5. Hydroxybiphenyl is esterified with benzoyl chloride to form the benzoate ester. This compound is then nitrated with fuming nitric acid. Selective recrystallization gives the 4-4' isomer. Hydrolysis of the ester gives 4-hydroxy-4'nitrobiphenyl sodium or potassium salt. Etherification of this biphenyl with the appropriate halo alkanol followed by reaction with methacroyl chloride produces the desired monomer.

FIGURE 3. NLO Side Chain Polymers First Generation

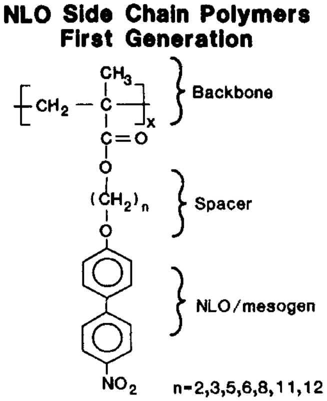
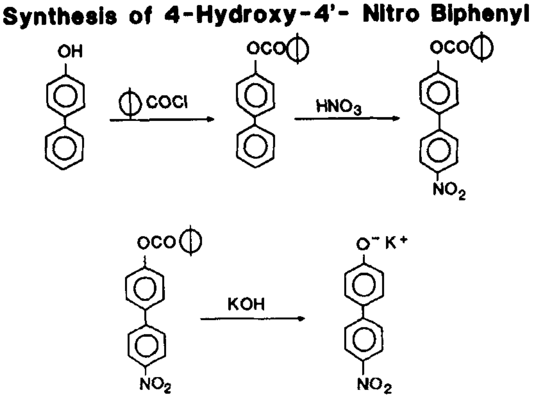


FIGURE 4. Synthesis of 4-Hydroxy-4'-Nitrobiphenyl



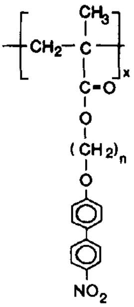
All polymerizations were conducted in toluene, with one mole percent of AIBN as initiator, at 60-80°C for approximately 16 hours.

The results found for the biphenyl polymers are reported in Table 2. For this series, a change in the LC order was observed as the spacer length increased. Moving the biphenyl unit away from the backbone reduces the influence the backbone exerts on the mesogenic unit and allows for more self-organizational freedom of the LC/NLO unit producing a more ordered phase. In fact, motion is so decoupled for the 11 and 12 carbon cases that crystallization of the side chain occurs when the polymers were cooled very slowly to ambient temperature. Unfortunately, as one moves the mesogenic unit away from the main chain, Tg decreases drastically. Although a more ordered smectic phase forms in the long spacer samples, the Tg is too low and externally induced orientation will decay over a period of time.

It appears that at moderate spacer lengths (5-6) where the Tg has a desirable value, the methacrylate backbone is stiff enough to change the order of the LC phase and a nematic results. A more flexible backbone at the same spacer lengths should allow a more ordered phase to form. To test this hypothesis, a side chain polymer composed of a nitrobiphenyl group with a 5 carbon spacer attached to a siloxane backbone was prepared (Figure 7). Although the Tg was low as is expected, the LC phase is a smectic A with a clearing temperature that is much higher than the corresponding methacrylate (165 vs. 72°C) indicating greater stability of the liquid crystalline phase (Figure 8).

TABLE 2. NLO Side Chain Polymer Properties

NLO Side Chain Polymer Properties



n	Phase	T_G (°C)	T_{cl} (°C)
2	I	-	-
3	N	85	100
5	N	45	72
6	N	40	64
8	N	35	75
11	S_A	20	95
12	S_A	10	80

I = Isotropic
N = Nematic
S = Smectic
T_G = Glass Temperature
T_{cl} = Clearing Temperature (LC ↔ Isotropic)

One of the primary premises of the NLO active polymer development effort was that the NLO activity of the polymers is the sum of the activity of the individual units despite the fact that they are now chemically attached to the polymer chains rather than being dissolved into the polymer matrix. To validate this hypothesis, the solvatochromic response of the NLO moieties and the NLO active polymers were determined and their NLO properties were evaluated. Comparison of the monomer and polymer data has shown that the NLO response was not altered to an appreciable extent in the polymerization[6].

FIGURE 5. Monomer Synthesis

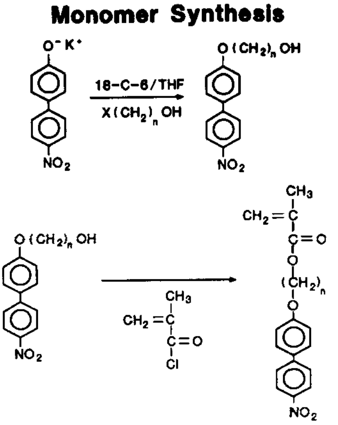


FIGURE 6. Dependence of Glass and Clearing Temperatures on Carbon Spacer Length

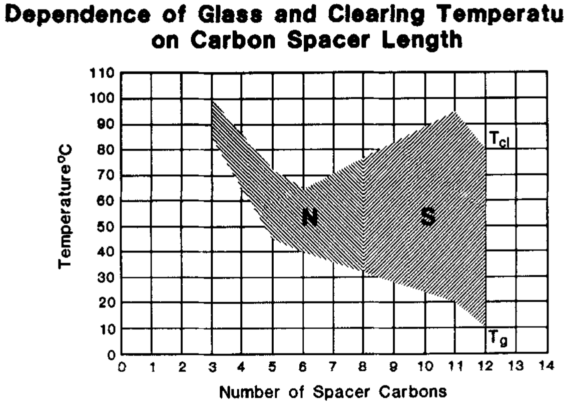


FIGURE 7. Siloxane Based NLO Polymer

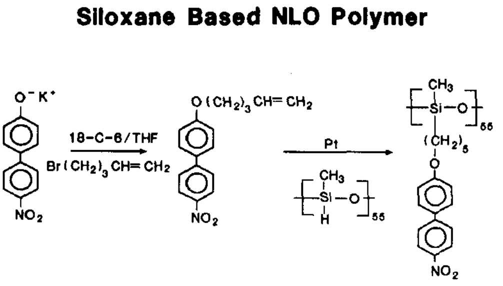
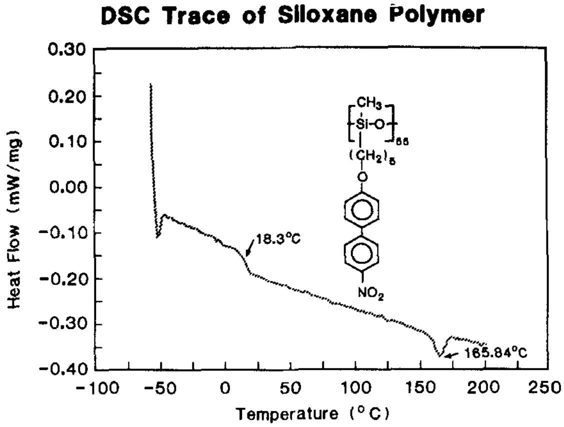

Siloxane Based NLO Polymer

FIGURE 8. DSC Trace of Siloxane Based NLO Polymer


DSC Trace of Siloxane Polymer

NLO POLYMER FABRICATION AND POLING

The poling experiments were largely carried out on 50-100 μm samples. Free-standing films were prepared by compression molding. Liquid crystalline polymer and other low MW guest/polymer samples were prepared by pressing the polymer melt between two conductive glass surfaces. Here, the sample thickness was controlled by spacers.

The free-standing samples were poled while held between 2.5 cm diameter brass electrodes. Typically, two layers of the samples were used to prevent premature dielectric breakdown due to pinholes in the samples. The samples and the electrodes were immersed in a constant temperature oil bath for both temperature control and to minimize surface dielectric breakdown. After the sample temperature was equilibrated to the bath temperature, an electrical field was applied across the samples by slowly raising the voltage to the desired level. The samples were kept at this poling condition, typically, for several minutes, taken out of the bath and rapidly cooled to ambient temperature before the electrical field was switched off.

Orientation of NLO liquid crystalline polymers can be demonstrated by applying an electric field to orient the liquid crystalline polymer creating an optically transparent monodomain material. As a result of the long range order of the liquid crystalline phase, defects are removed and the sample is transformed from a highly scattering opaque material to an aligned, optically clear $\chi^{(3)}$ material useful for nonlinear optics. $\chi^{(2)}$ materials may be created by applying higher DC fields as previously described[16].

DEVICES

NLO polymeric materials offer several distinct advantages for devices which can be divided into two general areas: intrinsic material properties and fabrication options. The intrinsic material properties have been well defined by single crystal NLO studies[17,18] and the generally known properties of organics. As has been highlighted, the NLO process for organics involves the polarization of loosely bound electrons in an organic molecule. This process is very fast (femtosecond) and lossless[19]. Both properties are quite unique. For example, nonlinear polarization of electrons in inorganic crystals is created in part by nuclear motion so that the tightly bound electrons move with the nuclei. This process is relatively slow. At very high frequencies (e.g. optical frequencies), the electronic nonlinearities are much smaller.

For GaAs or GaAs/AlGaAs multiple quantum well materials, a nonlinear change in the index of refraction is observed due to a nonlinear absorption process which involves the creation of electron-hole pairs[20]. However, there are significant absorption losses which lead to thermal heating.

NLO polymeric materials show a very slight dispersion in index of refraction (or dielectric constant) as a function of wavelength. For polymers, the dielectric constant at low frequencies is very nearly approximated by the square of the index of refraction at optical frequencies. This property is due to the disassociation of polarizable electrons from nuclei. For inorganics, the dielectric constant is much larger than this value. Thus, essentially all inorganic NLO materials have much higher dielectric constants than NLO polymers at electro-optical modulation frequencies. The implications for electro-optics are very significant.

The ultimate advantages of NLO polymeric materials are yet to be fully realized. Polymers may be processed in very unique ways. Thus, fibers may be created by spinning, thin films for waveguiding may be prepared by spin coating, varied objects may be formed by molding, etc.

These materials possess novel electro-optical properties and show low absorption loss and an optical surface flatness (as determined by interferometry) which is acceptable for many applications. As device applications using NLO polymers increase and the figure of merits become equal to those for inorganic NLO materials, the true merit of NLO polymer processing options will become readily apparent.

EXPERIMENTAL

Synthesis

Polymethacrylate Backbone

4-Hydroxy-4'-Nitrobiphenyl

(a) 4-benzoyloxybiphenyl

To 500 mls of pyridine in a 1000 ml three necked flask is added 170 g. of 4-hydroxybiphenyl. The mixture is cooled to 10°C whereupon 155 g. of benzoyl chloride is added dropwise keeping the temperature below 20°C. After complete addition, the mixture is gradually heated to reflux and held there for 30 minutes. The reaction is then cooled to 100°C and poured into a large beaker to cool. The hardened product is subsequently broken up with 250 ml HCl and 250 ml water. Then, an additional 250 ml HCl and 500 ml water was added and the whole mass mixed thoroughly in a blender. The solid is then filtered, washed with water to a neutral pH, and air dried overnight. Recrystallization is accomplished in n-butanol: mp 149-150°C.

(b) 4-benzoyloxy-4'-nitrobiphenyl

The above product (40 g) was mixed with 310 mls of glacial acetic acid and heated to 85°C. Fuming nitric acid (100 mls) was slowly added such that the temperature is kept between 85-90°C. After complete addition, the reaction is cooled to room temperature. The solid is filtered and washed with water and methanol. The product is then recrystallized from glacial acetic acid: mp 211-214°C.

(c) Hydrolysis of 4-benzoyloxy-4'-nitrobiphenyl

The above product (60 g) is mixed with 300 mls ethanol and heated to reflux. A solution of 40 g KOH in 100 mls water is then slowly added dropwise at reflux. After complete addition, the mixture is refluxed 30 minutes and cooled overnight. Next day, blue crystals of the potassium salt are filtered, washed with tetrahydrofuran until the wash is colorless, and dried. The salt is utilized in all subsequent reactions. Pure 4-hydroxy-4'-nitrobiphenyl can be obtained by dissolving the salt in a minimum amount of boiling water and adding 50/50 HCl/water until an acidic Ph is obtained. The yellow solid is then filtered, washed with water, dried and recrystallized from ethanol: mp 203-204°C.

Typical Prep of a Polymer with a 6 Carbon Spacer

4-(6-Hydroxyhexyloxy)-4'-Nitrobiphenyl

To 500 ml of toluene in a 1000 ml round bottom flask, fitted with a condenser and magnetic stirrer, is added 7.6g. (0.03M) of the potassium salt of 4-hydroxy-4'-nitrobiphenyl, 4.9g. (0.035M) of 6-iodo-1-hexanol, and 0.005 g. of 18-crown-6. The mixture is refluxed for 16 hours. Practically all of the potassium salt has reacted as evidenced by the absence of blue crystals. The solution is filtered hot and cooled to room temperature. After solvent removal, the solid residue was recrystallized from ethanol: MP 117-119°C.

4-(6-Methacryloxyhexyloxy)-4'-Nitrobiphenyl

The above product (22 g) is dissolved in 500 mls of dry dioxane and heated to 45°C. Triethylamine (14 g) is then added all at once. A solution of 10.5 g methacryloyl chloride in an equal volume of dioxane is slowly added dropwise keeping the temperature at 45°C. The reaction is then stirred at 45°C. After 4 hours, an additional 10.5g. of methacryloyl chloride is added and the mixture stirred overnight. The next day, the dioxane is removed under vacuum and the residue dissolved in water in a blender. The solid is filtered, washed with water, and air dried. The monomer is recrystallized from ethanol: mp 53-56°C.

Poly(6-[4-Nitrobiphenyloxy]-Hexyl)Methacrylate

The monomer (2 g) is dissolved in 20 ml degassed toluene and 1 mole% AIBN is added. The container is placed in a 60°C oil bath and heated 1 day. During this time, polymer forms and collects at the bottom of the container. After sufficient time (see text), the supernatant is poured off and the lower layer mixed with methanol in a blender. The solid polymer is filtered, washed with methanol and vacuum dried.

Polysiloxane Backbone

Poly[(4-Nitrobiphenyloxypentyl)Methyl]siloxane

Reactions are conducted in dry toluene at 60°C. Both materials are added such that there is a 10 mole% excess of biphenyl relative to the Si-H bonds. To this mixture is added 1-2 drops of chloroplatinic acid catalyst (5% weight/volume in isopropanol). After overnight heating at 60°C, the polymer is precipitated into methanol, filtered, and dried. Further purifications are carried out by dissolving in chloroform and precipitation into methanol until constant transition temperatures are obtained.

PHASE IDENTIFICATION

The phases exhibited by the side chain liquid crystal polymers were characterized in the following way. The temperature at which the isotropic to liquid crystal phase occurs is determined first. This is accomplished by optical microscopy using a Leitz Laborlux 12 pol polarizing microscope fitted with a Mettler FP-80 82 controller-hot stage combination. The Mettler controls the temperature to within 0.1°C and can be programmed to heat or cool at rates from 0.1 to 20.0°C per minute. The temperature is raised at 10.0°C per minute until the birefringent texture of the polymer, prepared on a microscopy slide, disappears. The temperature is then lowered at 5.0°C per minute until birefringence is regained. The Mettler is thus cycled up and down in temperature at slower rates of heating and cooling until the transition temperature is determined exactly. The oven is then set to cool into the liquid crystal phase from the isotropic state at 0.1°C per minute. Once some birefringence is seen optically, the temperature is held for long periods of time to allow the phase to anneal into its natural texture. Often, it is necessary to cool the oven in 0.2°C intervals every half hour to allow large domains to form in order to identify the phase. The textures that the side chain liquid crystal polymers exhibit have been found to be analogous to those shown by small molecule liquid crystal materials.

By taking these precautions, the probability of misclassifying the liquid crystal phase is low and problems of misidentification are avoided.

SUMMARY

The molecular structural characteristics which give rise to large optical nonlinearities have been delineated. This has been accomplished by several key steps and has led to the development of a structural algorithm for the design of β molecules with high susceptibilities. The molecular characteristics are:

a. Increased molecular length
b. Molecular planarity
c. Delocalized electronic structure (including connector units along the molecular long axis)
d. Asymmetric electronic environment using electron donating and attracting groups

Molecules combining all important structural features have been synthesized and characterized.

High activity molecular units have been covalently attached to form polymers which can contain up to 100% of the NLO moiety, and the resulting molecular optical properties have been characterized.

The second order molecular susceptibility was found to be undiminished by properly designed covalent bonding to form a polymer, and spectral characteristics were found to closely follow that of the NLO unit.

For the same backbone, Tg is influenced by the mesogen and the length of the spacer. Short spacers inhibit crystallization of the side chains, lead to less ordered structures and raise Tg. This is due to the large influence of the backbone. At these short spacer levels, no decoupling of main chain and side chain motions is possible. A less but still profound influence is exerted by the main chain on mesogen organization at intermediate spacer lengths. More rigid chains (polymethacrylate and polyacrylate) lead to less ordered structures. Flexible chains (polysiloxanes) lead to more ordered states. Tg is lowered in the polysiloxane series relative to the methacrylate series over polymers with shorter spacers. Complete decoupling of the main chain and side chain motions occurs in polymers containing long spacers resulting in the most ordered structures for this series. However, Tg is the lowest for this series. Due to this decoupling, side chain crystallization occurs.

Control of orientation has been achieved by applying external fields.

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