Polymeric materials for second-order nonlinear optical applications

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1. INTRODUCTION:

Polymers that contain nonlinear-optical (NLO) moieties are considered to be promising for the development of phtotonic devices.[1-5] This expectation is based on the fact that NLO polymer can display higher NLO coefficients than that of inorganic crystalline materials currently in use and the indisputable facts that polymers are much easier to process, possess lower dielectric constants, can be lithographically patterned, and are more compatible with integration of optical and semiconductor devices. The purpose of this paper is to give a brief review of polymers for second-order nonlinear optical applications.

2. POLYMER SYSTEMS

2.1. Guest-host system[6]

Three major kinds of polymers have been studied for second order NLO effects, i.e., guest-host system, side chain and main chain polymers. The simplest approach to poled polymer NLO material is the use of polymer solutions, or guest-host systems where there is no chemical bonding of the NLO chromophores to the polymer backbone, and the chromophores are just dissolved in the polymer matrixes. The special merit of guest-host systems for NLO applications is that the preparation process is very simple, one only need dissolving the guest molecules and host polymers in a suitable solvent. However, the amount of NLO molecules that can be dissolved in host polymer is limited in most cases to about 10%, the low solubility of the chromophores in the polymer matrix may result in segregation of crystals of the guest, which is detrimental for the film quality and induces large optic loss due to scattering. Even before actual segregation of crystals occur, aggregates may be formed. Moreover the most important disadvantage of these guest-host systems is the very poor temporal stability of the polar orientation by thermal randomization processes. Recently, some guest-host systems with relatively good temporal stability by using high Tg polyimides as host matrixes have been reported.

2.2. Side chain polymer[7]

Compared with guest-host systems, dye-grafted polymer systems have been found to be more effective because they offer several advantages over the guest-host systems such as: a higher molar concentration of the NLO species; increased orientation stability; and better film homogeneity and so on. These advantages make it more interesting over the guest-host polymer mixture. Recently, dye grafted polyimides with excellent thermal and temporal stability of poling induced orientations have been reported.

Side chain polymers have significantly more stability of the electric field poling induced nonlinear optical effects than those of guest-host polymers, but still suffer from slow relaxation of field induced noncentrosymmetric alignment (β relaxation at lower temperature) and hence the nonlinearity.

2. 3 Main chain polymers

Progressing from guest-host system, to side chain polymer, one arrives at another class of materials were the dipole is part of the polymer backbone, i.e. main chain polymers. If alignment of main chain polymer could be achieved, the energy of activation for randomizing the system would be extremely large and the system would be quite stable. Several types of main-chain polymers have been proposed for second-order NLO applications, such as head-to-tail[8] structure, accordion conformation, and Λ-type charge transfer chromophores.

The earliest studied main-chain polymers consisted of chromophores with their dipole moments oriented "head-to-tail" along to the polymer chain. It was expected that this head-to-tail arrangement of the molecular dipole moments might results in a coherent enhancement of the second-order nonlinear properties. However, till now, only one such kind head-to-tail main chain polymer was reported can be poled by corona discharge.[8]

A variation to the head-to-tail main chain polymer was recently reported by Lindsay and co-worker.[9] In this strategy the polymer backbone is folded into an accordion shape. In these polymers, the long axes of the rigid chromophoric units are essentially perpendicular to the axis of the polymer chain, the bridging groups are generally U-shaped connections. One of such shaped polymer L-B films is not SHG active, but a poled polymer with similar structure has d_{33} about 5 pm/V.

A new molecular design strategy, i.e., Λ-shaped charge transfer molecules for SHG, was proposed. This strategy could more easily induce noncentrosymmetric structures and optimize the phase-matchable NLO coefficients. To prove this new molecular-design idea, both theoretical calculations as well as experiments have been done on model compounds in our laboratory.[10] In an Λ-shaped molecule, the intramolecular charge transfer contributing to β has almost a two-dimensional character and the off-diagonal components of the hyperpolarizability (β) are large. Such kind large off-diagonal components are necessary to increase the effective phase-matched harmonic generation. However, similar to other organic materials, the crystal growth of Λ-shaped molecular materials with large size and high optical quality is also not easy. Therefore, we think if Λ-shaped chromophores can be incorporated into polymer backbone, the obtained main-chain polymers should be effectively oriented by corona poling due to the two-dimensional charge transfer structure of the chromophores. The first series of main-chain polymers with Λ-shaped chromophores are polyarylamines[10(b)] prepared by the reaction of bis(4-fluoro-3-nitrophenyl) sulfone (BFNPS) with both aliphatic and aromatic diamines.

Developing polymers with high glass transition temperature is one of the main methods to improve the thermal and temporal stability of poling induced polar alignments. The other extensively studied method is to decrease polymer mobility via thermal or optical cross-linking.[11] The effectiveness of this method is due to the formation of inter-chain chemical bonds and depends on the number, nature, and sites of cross-linking. However, this method often inducing other problems such as polymer insolubility, optic loss due to light scattering, embrittlement, shrinkage, etc. These fabrication difficulties are exacerbated for optic device applications.

3. NEW FILM FORMING TECHNIQUES

Polymer films are usually prepared by spin coating of polymer solution. The proper solubility of polymer in general organic solvents is a prerequisite for the achievement of high quality films. Furthermore, the intimate association of processing to the rheological properties of the polymer solution creates difficulties in film thickness and uniformity control.

Vapor deposition polymerization (VDP)[12] offers an alternative process of fabricating polymer thin films. Since this is a dry process, films produced by evaporation do not exhibit the rheological effects and solvent retention of solution cast film. The polymer deposition system consists of two evaporate sources and the effusion rate of each oven can be controlled independently. The individual vapor streams are combined in a buffed mixing oven produce a single homogeneous vapor stream then reaction and polymerization on substrate. From the processing point of view the main merits of VDP method, compared with conventional methods, offers an advantage not only of greatly decreasing the amount of impurities in a film as a result of vacuum deposition, but also of rigorously controlling film thickness. In addition, VDP presents the possibility of obtain molecular-oriented thin films with properly setting of the evaporation rates of monomers, substrate temperature and annealing conditions.

The dry-processing techniques (VDP) have some merits over wet-processing techniques, however, to date, only a few polymers can be formed by these methods and further more research is necessary.

Molecular self-assembly[13] is the spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates joined by noncovalent bonds. This technique has been widely used in forming complex biological systems and in organic synthesis for nanostructures. Molecular self-assembly has also been used as an alternative method to forming noncentrosymmetric structures for NLO applications.

4. PHASE-MATCHING METHODS

Poled polymers have many merits over single crystals for second-order NLO applications. Nevertheless, to find commercial applications two big problems are still exist for these materials: one is the relaxation of the poling induced orientation as discussed at above sections, the other one is the difficulty in realizing effective phase matching between fundamental and second-harmonic waves. In a second harmonic generation (SHG) process, phase-matching is the first important condition to get high SH conversion efficiency. A general method is using the natural birefringence in certain anisotropic crystals to compensate the refractive index dispersions between the fundamental and second harmonic wavelengths.

The reported phase-matching methods in poled polymers include mode dispersion method; [14] quasi-phase matching (QPM);[15] Cerenkov radiation method;[16] non-collinear phase-matching[17] and the use of birefringence.[18]

Mode dispersion phase-matching is based on the fact that waveguides generally support several modes, each with a different propagation constant, i.e., a different effective refractive index $N_{eff}=n_f \sin\theta$. This index is lower for the higher order modes and therefore PM $(n^{\omega}_{eff}=n^{2\omega}_{eff})$ can occur if the fundamental wave propagates in a lower order mode than the generated second-harmonic (SH) wave. To realize this type phase-matching, the film thickness should be accurately controlled to several nanometers.

QPM method involves repeated inversion of the relative phase between the forced and free waves after an odd number of coherence lengths, or periodically poling the film. This method has wide applicability, nevertheness, to accurately control the periodicity in thin film is very difficult, especially for poled polymer.

The Cerenkov radiation method can significantly relax the phase-matching conditions, but the generated SH wave front in Cerenkov radiation is conical. Therefore, a special lens is necessary to focus the SH light. Such lens will increase the complexity of device structure. Furthermore, the conversion efficiency of Cerenkov radiation phase-matching in principal is less effective than that by mode-to-mode phase-matching.

It was believed that phase-matching in poled polymers by the use of birefringence is not possible since we can not realize $n_{\omega}=n_{2\omega}$. [19] However, we found it is possible to realize bulk phase-matching in drawn and poled main-chain polymers with Λ-type charge-transfer chromophores.[18] Compared with other methods used in poled polymer films, the bulk phase-matching has the following characteristics: (1) In modal dispersion phase-matching or quasi-phase matching, accurate film thickness or periodicity control is necessary. This is difficult for poled polymers. However, there is no such requirement in bulk phase matching. Therefore the preparation process is simple. (2) For other phase matching methods, the conversion efficiency not only is related to the nonlinear coefficient, but also proportional to the square of spatial overlap integrals between the fundamental and second-harmonic waves. The overlap integrals between different modes are small and will significantly decrease the conversion efficiency obtainable. In birefringence phase matching there are no such effects. (3) The refractive indices of single crystals are determined by their constituents and structures. Therefore it is not possible to engineer a single crystal with the expected birefringence. However, one can adjust the refractive indices of the poled polymers by varying draw ratio. At a certain draw ratio noncritical phase matching may be realized. In this case a longer phase-matching interaction length can lead to a higher SH conversion efficiency.

The recent achievements of polymeric materials in EO applications are summarized in several excellent review papers.[20, 21]

5. CONCLUSION

Polymeric materials can be formed into efficient second-order nonlinear optical materials. These materials simultaneously take advantage of the large optical nonlinearity of the conjugated chromophores and the favorable optical, mechanical and dielectric properties of the polymer glasses. Over the years, our understanding of second-order NLO materials has advanced dramatically and poled polymers with nonlinearities as large as state-of-the-art inorganic materials have been reported. However, the use of second-order nonlinear polymers in devices still awaits solutions to a number of problems. Key among these is the thermal stability, both long term and short term. Other parameters are not generally reported but must be carefully understood and controlled for poled polymers include: stress-induced birefringence and its temperature dependence, thermal coefficients of expansion, electro-migration effects, and other parameters. In summary, numerous researches have been done to put poled polymers for practical applications, and the future of this technology depends on the joint efforts of material scientists, device designers, and process engineers. If we can build "best of the bests" all into one system, the new devices based on polymers should be commercially available in the near future.

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