

Preface

Within the framework of electromagnetic radiation interaction, nonlinear optics is a subject covering a series of phenomena in which incident radiation is altered in its frequency, phase, or amplitude while interacting with a medium. Since its birth, linked to the discovery of the laser in 1960, nonlinear optics and photonics have been interrelated, where photonics is understood as the set of technologies that use photons to process information. Typical nonlinear phenomena, such as frequency conversion or optical modulation, have been the key to the development of photonic technology.

Notwithstanding that any material may show nonlinear behavior, there is a list of unquestionable requirements concerning applications. The search for materials showing high and stable nonlinear response, good processability, and, moreover, thermal and photochemical resistance has aroused great interest. At first, the investigation was focused on inorganic materials, which led to results relatively quickly; nonlinear crystals (e.g. KDP, KTP, and BBO) were incorporated in commercial systems and they are often found in frequency doubling and tripling or as parametric oscillators in tunable lasers.

Although organic materials appeared in the 1970s, it was during the 1980s and 1990s that interest in this line of investigation increased hugely. One of the reasons for this was their synthetic versatility, which allows molecules to be designed with specific properties, in particular, with very large nonlinear response. Parallel to the optimization of the nonlinear response, the need to transfer of these large responses efficiently to the macroscopic scale was also highlighted. It seems clear, therefore, that the investigation and development of organic materials for nonlinear optical applications need to use molecular engineering to design and synthesize efficient molecular moieties and materials engineering to achieve macroscopic systems with a molecular arrangement that assures a high nonlinear response.

The difficulty of preparing organic crystals with good quality (moreover, many applications require the absence of centrosymmetry) drew attention to polymeric materials, given their easy processability, fast response and, generally, lower cost. The incorporation of nonlinearity in polymers can be achieved by dispersing nonlinear molecules in them (*guest–host* systems) or by attaching them to the polymer chain chemically, often as side groups. In any case, the mentioned noncentrosymmetric arrangement requires the polymers to be able to be ordered polarly, usually

by an electric field that orients molecular dipoles. Unfortunately, many of the most efficient nonlinear molecules have large dipole moment values, promoting molecular interactions that give rise to centrosymmetric structures and thus yielding a nonlinear response poorer than expected. In recent years, one of the objectives in the design of polymeric guest–host systems for electro-optic applications has been to decrease these interactions, while maintaining a high content of chromophore and to look for structures that contribute to stabilizing polar orientation.

Side-chain polymers, in turn, allow a higher chromophore content to be included while avoiding phase separation and they offer better stability in the induced order, particularly when high glass transition temperature (T_g) polymers are used if the orientation process takes place at very high temperatures. As an alternative way to force chromophore orientation, promoting the stability of the established order, the use of liquid-crystalline polymers has been proposed. In these kinds of systems, very anisotropic nonlinear responses have been reported, but the effect of chromophore interactions upon the global nonlinear response magnitude has not been so widely studied. Part of the work presented here falls within this line. The nonlinear response of a number of homo- and copolymer-ethacrylates showing nematic and smectic phases has been studied. Nonlinear chromophores in the side chain, besides having promesogenic nature, include photo-orientable azo groups, which has enabled their orientation to be modified optically and its influence on nonlinear response to be studied. On the other hand, they offer the possibility of using photoassisted processes to orient polarly with an electric field, allowing breaking of centrosymmetry at temperatures well below T_g , owing to the increase in the mobility induced by light. Furthermore, the applied selective illumination in this process leads to nonlinear gratings, which combine an efficient second harmonic generation in thin film configuration with a spatial filtering of 2ω light.

In [Chap. 1](#) of this report, some theoretical concepts and material characteristics (chromophores and liquid-crystalline polymers) on which this thesis is centred are reviewed.

In [Chap. 2](#), devoted to the experimental details, the techniques used to characterize linear and nonlinear optical properties of molecules and thin polymeric films, as well as the experimental data analysis methods, are thoroughly described.

The second-order nonlinear response results, obtained from EFISH (electric field-induced second harmonic) technique measurements for several families of compounds are gathered in [Chap. 3](#), as well as a discussion of these results.

The two following chapters are focused on the nonlinear properties of polymeric films oriented by an electric field. [Chapter 4](#) describes a series of copolymers with different nonlinear and photo-orientable chromophore content in the side chain. The nonlinear response, which can be controlled by thermal and optical treatments, is analyzed by means of second harmonic generation measurements, as a function of the chromophore content. In [Chap. 5](#), in turn, the nonlinear response of highly efficient chromophores mixed with photo-orientable polymers with a slight response is described, proving that polar photoassisted orientation techniques can be extended to these kinds of systems. Moreover, the coupling between

the induced order in the polymeric matrix (by light irradiation or heating) and the order achieved by the dispersed chromophores is investigated.

Finally, in [Chap. 6](#) diffraction grating formation is described in azopolymers with donor- π -acceptor chromophores. Furthermore, NLO properties were induced in the mentioned gratings and second harmonic diffraction efficiency was characterized as a function of different parameters, as the amplitude of the surface relief or the different NLO response characteristic of each polymer.

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