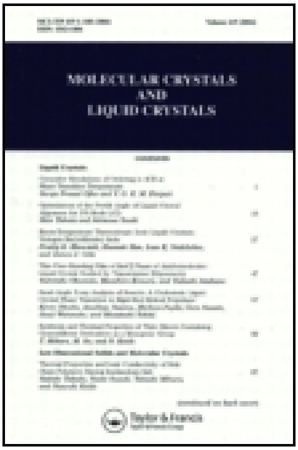

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Nonlinear Optical Polymers: Design of Tougher NLO Polymers Using Chain Parameters Structure and Processing Issues of Thin Film

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STRUCTURE AND PROCESSING ISSUES OF THIN FILM NONLINEAR OPTICAL POLYMERS: DESIGN OF TOUGHER NLO POLYMERS USING CHAIN PARAMETERS

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Abstract One of critical problems in the preparation of electro-optic devices from NLO polymers is their brittle nature and tendency to form cracks during the device fabrication process. In order to design a new NLO polymer with improved toughness, a computer modeling study has been carried out developing correlations between molecular parameters and toughness of polymers. When polycarbonate instead of PMMA is used as a backbone chain for the NLO polymer, a significant improvement in toughness of NLO polymers are found. This finding suggests an important strategy in designing a new NLO polymer because the cracking problem can be eliminated without sacrificing any other necessary requirements for NLO materials.

INTRODUCTION

Recently, organic nonlinear optical (NLO) polymers have emerged as a rapidly developing research area since they possess a number of important characteristics for NLO device applications such as large nonlinear susceptibility, fast response time, low dielectric constant, and easy processability. Much research has focused on the development of polymers with a large NLO activity and high poling efficiency. However, for successful implementation of device applications, the NLO polymers must satisfy other material characteristics, such as good mechanical properties, optical transparency, and thermal and photostabilities.

The formation of cracks in NLO polymer films during a device fabrication process has been a serious problem. In order to fabricate an optical device, the cracks in the films have to be completely eliminated. The reasons of the crack formation in the thin NLO polymer films has been discussed in detail with some potential solutions of the problem in our previous paper.[1] Other important properties necessary for device-worthy NLO materials are low optical loss and optical stability at the operating communication wavelength, 1.3 μm. These are critical material properties when waveguide devices made of NLO polymers are employed in the communication systems. The relations between structures of NLO polymers and optical loss[2] and optical stability[3,4] have been discussed elsewhere in detail.

In the present paper, we investigate the nature and causes of cracking in NLO polymer films and find a design rule of a new side chain NLO polymer with mechanically tougher characteristics. Molecular parameters affecting mechanical properties of polymers have been studied based on a pseudo-topological model of polymer entanglements.[5] With an understanding of correlations between molecular parameters and toughness of polymers, a modeling study was carried out to find mechanically tougher NLO polymers.

The efficient design of new polymer molecules requires a prediction of properties of many candidate polymers prior to synthesis. These predictions can be used to evaluate, screen, and prioritize the synthesis of the candidate molecules. Many empirical group contribution methods have been proposed to correlate properties of polymers with chemical structures.[6] However, the polymers for NLO applications requiring a large polarizability change usually contain exotic structural units to which most group contribution techniques cannot be applied. Some of the required group contribution parameters are often not available, and there are no previous experimental data available in estimating missing group contribution parameters. This difficulty could be overcome by using a new method of calculation in which the properties are expressed in terms of topological variables.[7] A computer program Synthia (from Biosym Technologies, Inc.) utilizes this methodology and enables prediction of the properties of novel polymers by the summation of additive contributions over atoms and bonds instead of groups. Several important chain parameters and the structure-property relationships in NLO polymers are investigated by using a computer modeling study. By understanding the trends of brittleness in polymers with different size of backbones and pendant groups, we can suggest directions for the synthesis of new NLO polymers with improved toughness.

STRUCTURE AND TOUGHNESS OF NLO POLYMERS

One of critical problems in the preparation of electro-optic devices from NLO polymers is their brittle nature and tendency to form cracks during the device fabrication process. The brittle nature of most side chain NLO polymers is originated from characteristics of the low molecular weight and the absence of the secondary relaxation. Such characteristics are inherent to NLO polymers due to the chemical nature of the NLO chromophores. A reason for NLO polymers having a low molecular weight can be found in their polymerization mechanism. Most NLO polymers are prepared by a radical polymerization reaction, NLO chromophores act as reaction inhibitors or retarders suppressing the polymerization of monomers. The nitrobenzene and amine groups which are found in most NLO chromophores are used as typical reaction retarders which react with the initiating or propagating radicals and convert them into non-reactive species.

Besides the influence of the molecular weight, another significant structural factor that affects polymer toughness is the presence of secondary relaxation in a polymer chain. It is generally accepted that ductile polymers have pronounced low temperature secondary relaxation processes. Because of other requirements for the chromophores in nonlinear optical applications, it is, however, difficult to design NLO polymers having such secondary relaxation. The NLO chromophores usually consist of several stiff benzene rings and have a planar structure to enhance conjugation of π-electrons along the chromophore. Due to a rigid structural characteristic of the NLO chromophore, it is thus inherently difficult for NLO polymer chains to have the secondary relaxation, as noted in our previous paper[1] on dynamic electric thermal analysis experiments of NLO polymers.

Chain entanglement is a critical factor controlling mechanical brittle/ductile behavior of polymers since toughness of polymers increases with the chain entanglement density. A number of empirical relations have been proposed to relate the entanglement behavior to chain structure. Wu proposed[5,8] a pseudo-topological model in order to describe the entanglement behavior which was determined by chain tortuosity. The chain length between entanglement junctions is proportional to the square of the chracteristic ratio of a coiled chain in this model. Since the characteristic ratio is a measure of the steric hindrance to skeletal bond rotation and thus the intrinsic flexibility of chain, this model indicates that the number of entanglements per unit volume, i.e. entanglement density, increases with polymer chain flexibility. Other empirical equations[9-11] have been proposed for correlating the entanglement behavior with the cross-sectional area of a chain. It was reported[9] that the entanglement molecular weight increases with volume of the pendant groups since steric hindrance to skeletal bond rotation becomes larger as the size of pendant groups increases. In many empirical correlations, the chain entanglement behavior was related to chain structure through the average chain thickness or the characteristic ratio. These chain parameters and the entanglement chain length are used to investigate the effect of the chain parameters on toughness of polymers.

COMPUTER MODELING STUDY

The chain and entanglement parameters have been calculated and listed in Table I for polymethylmethacrylate (PMMA) and polycarbonate together with two NLO polymers which have different backbones (PMMA and polycarbonate) with the same 4,4-dimethylamino-4'-nitrostilbene (DANS) side chain chromophore. PMMA-DANS is a 50/50 MMA/MMA-DANS copolymer which is a typical NLO polymer used in the current NLO device fabrication process. PC-DANS denotes an NLO polymer with polycarbonate backbone and a DANS side chain. It is not surprising to see that polycarbonate which is known as a tough engineering plastic has a very small characteristic ratio and thus having a smaller entanglement chain length (i.e. higher entanglement density) compared to PMMA. It is thus expected based on this calculation that polycarbonate has higher fracture energy than PMMA. As an approximate measure of the fracture energy, impact strength (1/8 inch thick specimen) of polymers are compared for PMMA and polycarbonate in Table I.

The NLO polymer PMMA-DANS has a large characteristic ratio indicating very brittle characteristics since it has a smaller number of entanglements per unit volume. Therefore, when a device is fabricated with this NLO polymer, the problem of cracking should be encountered during the thin film fabrication process. When the backbone chain of the NLO polymer is replaced from PMMA to polycarbonate, i.e. PC-DANS, it is found that the caracteristic ratio decreases

Table I. Chain parameters and impact strength of polymers

Polymer	Characteristic ratio	Entanglement length (Å)	Impact strength (ft.lb/in)
PMMA	8.3	302	0.2 - 0.4
Polycarbonate	3.3	129	12 - 16
PMMA-DANS	12.1	590	
PC-DANS	4.1	191	

significantly and resulting an increase of the entanglement density. The entanglement chain length of PC-DANS is even shorter than that of PMMA. This indicates that toughness of PC-DANS polymer may be better than that of PMMA with which we could fabricate multi-layered film structures without having the cracking problem. This finding suggests an important strategy in designing a new NLO polymer. By preparing polycarbonate based NLO polymers, the cracking problem can be eliminated without sacrificing any other necessary requirements for NLO materials because optical transparency of polycarbonate is as good as PMMA and the glass transition temperature of polycarbonate is high enough for the successful poling process.

CONCLUSIONS

The ability to predict the key physical properties of a polymer from its molecular structure is of great value in the design of a new polymer molecule. It is thus effective in designing of NLO polymers based on a prediction of the critical properties of new candidate polymers prior to synthesis. A computer program was used to calculate chain and entanglement parameters of NLO polymers in order to develop correlations between molecular parameters and toughness of polymers. When polycarbonate instead of PMMA is used as a backbone chain for an NLO polymer, a significant improvement in toughness of NLO polymers are found. Having DANS as a side chain chromophore, the polycarbonate based NLO polymer shows a much smaller entanglement chain length compared to the PMMA backbone polymer with the same NLO chromophore, even smaller than that of PMMA. This finding indicates that the fracture stress of the side chain NLO polymers can be considerably enhanced by changing the backbone structure. This improvement is attributed to the fact that polycarbonate backbone polymers have larger number of entanglement densities than PMMA backbone polymers, thus leading to enhancement of toughness and mechanical strength of the polymers. Therefore, it is evident that such an increase in the entanglement density is an important factor in the design of new NLO polymers which do not exhibit cracking during the device fabrication process.

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