

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

PREVIEW

Order Number 9430169

Second-order nonlinearity studies on organic polymeric materials

Guan, Hann-Wen, Ph.D.

The University of Nebraska - Lincoln, 1994

Copyright ©1994 by Guan, Hann-Wen. All rights reserved.

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

PREVIEW

SECOND ORDER NONLINEARITY STUDIES ON
ORGANIC POLYMERIC MATERIALS

by

Hann-Wen Guan

A DISSERTATION

Presented to the Faculty of
The Graduate College at the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy

Major: Chemistry

Under the Supervision of Professor C. H. Wang

Lincoln, Nebraska

April, 1994

DISSERTATION TITLE

SECOND ORDER NONLINEARITY STUDIES ON ORGANIC POLYMERIC MATERIALS


BY

Hann-Wen Guan

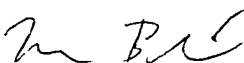
SUPERVISORY COMMITTEE:

APPROVED


DATE


Signature
Dr. Chin Hsien Wang


4/28/94

Typed Name

Signature
Dr. William H. Braunlin

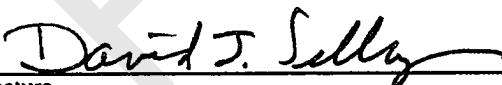
4/28/94

Typed Name

Signature
Dr. Craig J. Eckhardt

4/29/94

Typed Name

Signature
Dr. Gordon A. Gallup

4/27/94

Typed Name

Signature
Dr. David J. Selmyer

4/29/94

Typed Name
Signature
Typed Name



SECOND ORDER NONLINEARITY STUDIES ON ORGANIC POLYMERIC MATERIALS

Hann-Wen Guan, Ph. D.

University of Nebraska, 1994

Adviser: C. H. Wang

Second order nonlinear optical (NLO) properties of organic polymer thin films were studied by optical second harmonic generation (SHG) and electrooptical measurements. The polar orientational order parameters (POP) were deduced from the second order susceptibilities and from the first order electrooptical coefficients. It is found, in the guest/host system, that the POP is NLO chromophore concentration and external electric poling field dependent. By monitoring the *in situ* SHG intensity change, we are able to study the temporal stability of the polymer systems under different preparation and different poling conditions. The decay of SHG signal is found to be affected by surface/trapped space charges as well as polymer chain conformational changes induced by the electric field. It is shown that reproduceable relaxation experiment can not be obtained unless the sample has been successively poled. In guest/host systems at temperatures above the glass transition temperature (T_g), a two single exponential decay function is found to give a good fit to the SHG intensity decay curve. On the other hand, the SHG intensity decay curve from a main-chain polymer system is found to follow a Kohlrausch-Williams-Watts (KWW) equation.

It is also shown that above T_g , the temperature dependence of the steady-state average relaxation time is not Arrhenius; the Vogel-Fulcher-Tammann equation gives a satisfactory fit to the temperature dependence data. It is shown that the SHG relaxation is different from that obtained by birefringence, dielectric, or absorption recovery techniques. The SHG technique is also successfully applied to investigate the physics of pure blank polymers in the presence of a high electric field. Finally, the Mach Zehnder interferometry technique has also been used to determine the Pockels and Kerr coefficients.

PREVIEW

Acknowledgements

At this moment I feel like I am standing on the top of a big mountain - I am so small and yet mountain after mountain sits out there, waiting for me to explore them. Without the encouragement and love from my parents, I could never have reached this point. I have met many wonderful people and have enjoyed this incredible experience.

I am grateful to my advisor, Professor C. H. Wang, who has guided me in becoming an experimentalist in physical chemistry. He has inspired me and guided me to this final stage. His enthusiasm towards science, his courage in difficulties, and his profound intuition in physics, have set a high standard which I will try to live up to throughout my life.

I would like to give my special gratitude to Janelle Jonse, our secretary. Her hugs and listening ears have and will continue to comfort me.

I especially thank Dr. Walter Hancock, Jonathan Skean, Leslie Marquart and Dr. Kurt Wulser, from whom I have gained precious knowledge about electronics, computers, and machinery.

I would also like to thank someone I never met, Dr. Dominique Morichere, who provided me with detailed information on the "Reflexion Totale Attenuée" project. His generosity and enthusiasm are deeply buried in my heart.

My thanks is extended to Michael Cook and Kathy Thompson for their good-natured support.

I own special thanks to Mark and Maria Pauley, my partner in the laboratory and friends to our family; Mark has read through my thesis word by word and has corrected a great many grammar and spelling mistakes.

I thank all the members of the Wang group. Dr. Jin Fan Zhang, Sihong Gu, and Xuanqi Zhang, those working hard visiting scholars, who had worked with me and shared my frustrations and success. Ted Goodson III, Okeung Song, Jenhwa Sun, and Chinron Huang have all made their contribution to make our group a stimulating environment.

I would also like to thank all my friends from the beautiful island of Taiwan. I have enjoyed their friendship and will cherish it for many years to come.

To my dear wife Horng-Yuh Lee, what I can say? I love you!

PREVIEW

善哉

PREVIEW

Table of Contents

Abstract

Acknowledgments

I.	Generation Introduction.....	1
	References.....	8
II.	Dipolar Interaction Assisted Effects on SHG.....	10
	A. Introduction.....	10
	B. Experimental.....	12
	C. Results and Discussion.....	15
	D. Conclusion.....	23
	E. Appendix.....	24
	References.....	29
	Figures.....	31
III.	Poling Dynamics and Relaxation of Polar Order in Guest/Host Polymers by Second Harmonic Generation.....	39
	A. Introduction.....	39
	B. Experimental.....	41
	C. Results and Discussion.....	44
	1. SHG Intensity and Poling Field Strength.....	44
	2. SHG Intensity Relaxation and Surface/Trapped Charges....	48

3. Isothermal Annealing and Memory Effect.....	55
4. Dipolar Relaxation and Temperature Effect.....	58
5. Dipolar Relaxation and Poling Field Strength Effect.....	60
D. Conclusion.....	65
E. Appendix.....	67
References.....	68
Figures.....	70
IV. Second Harmonic Generation study on the Main-Chain Polymer.....	89
IV-1. Accordion NLO Polymer.....	89
A. Introduction.....	89
B. Experimental.....	92
C. Results and Discussion.....	93
1. The $\chi^{(2)}$ value.....	93
2. SHG Intensity Relaxation.....	97
3. Optical Anisotropy.....	101
D. Conclusion.....	107
IV-2 Pure Bulk Polymers.....	107
A. Introduction.....	108
B. Experimental.....	109
C. Results and Discussion.....	110
D. Conclusion.....	114
E. Appendix.....	116

1. Raman Shifter Condition.....	116
2. Structures.....	117
References.....	119
Figures.....	122
Table.....	139
V. ElectroOptic Measurements of Dye/Polymer Systems.....	140
A. Introduction.....	140
B. Experimental.....	142
C. Results and Discussion.....	147
D. Conclusion.....	151
E. Appendix.....	152
1. Structures.....	152
2. Pockels and Kerr coefficient from MZ.....	153
References.....	158
Figures.....	159

I. General Introduction

Photonic systems offer the possibility of extremely high speed signal processing, transmission and data storage. To realize this possibility, one requires high-performance nonlinear optical (NLO) materials, particularly those exhibiting second-order NLO effects. Certain conjugated organic molecules have been known to exhibiting substantial second order optical nonlinearities and are candidates for the high-performance photonic materials. Because of this synthetic organic chemists have been engaged in preparing conjugated molecules with high optical nonlinearity. Although synthesizing and assembling new molecules with larger nonlinear optical responses are of great necessity, gathering sufficient knowledge of the physical properties on the bulk assembly is essential for converting the test tube miracle to the real world product.

Due to their potential applications in integrated optics, interest in organic NLO materials has grown rapidly during the past decade.¹ Organic polymeric materials have lower dielectric constant, compared to the LiNbO_3 and GaAs class of inorganic materials,² which can significantly enhance the signal coupling efficiency. Due to ease in processability as well as considerable durability and flexibility, polymeric materials, either doped or covalently bonded with NLO chromophores, have been considered as promising candidates for photonic applications.³ In order to exhibit the second order effect, not only must the

molecule have a large second order susceptibility, but the bulk assembly can not have a center of inversion symmetry. In isotropic NLO materials the effect responsible for the electro-optic response and second harmonic generation can be induced by a strong external electric field, by which the macroscopic center of inversion symmetry is removed. The external electric field polarizes the sample, and creates polar order in the amorphous polymer system. To accomplish this, an electric field is usually applied at a temperature higher than the glass transition temperature (T_g) of the polymer, at which the polymer host provides a mobile environment to allow the dipoles to reorient. Under the influence of the strong external electric field, the dipoles of the NLO chromophores orient along the electric field direction. Maintaining the electric field, by slowly cooling below T_g , and then removing the electric field at the end, will freeze in the induced polar order in the medium. Thus, by incorporating these molecules into the polymer system and then polarizing them with a strong DC electric field to remove centrosymmetry, one can prepare a second-order NLO material. The electric field polarizing process is known as “poling”.

In addition to the electric field poling technique to process the NLO polymers, at AT&T Bell Laboratories Katz *et al.*⁴ used a two step process to deposit an inorganic interlayer next to a NLO organic chromophore. They successfully packed up to 30 layers of selfassembled film onto a zirconium phosphate layered surface.⁴ By utilizing silicon chemistry, Marks and coworkers⁵ were able to directly synthesize NLO organic chromophore onto a

glass substrate. They obtained a multilayered covalently bonded NLO chromophore assembly in the desired direction.⁵

Immediate device applications rely on the linear electro-optical (e-o) effect, that is, modulation of the refractive index depends linearly on an external electric field. Using the linear e-o effect, Mach-Zehnder modulators made from organic polymeric materials⁶ capable of operating at tens to hundreds GHz have been demonstrated by several research groups.⁷ An optical switch, working as a light valve for projection display, has also been shown by Takizawa's group in Japan.⁸

However, problems concerning thermal and temporal stability must be solved in order to utilize the potential of organic NLO polymers.⁹ IBM's group has used NLO chromophores epoxide crosslinked at desired temperatures to improve on the temporal stability. At the Naval Weapons Center, Lindsay's group has synthesized a main-chain NLO polymer which has a T_g of about 200°C.¹⁰ At Lockheed Corporation, Lytle's group,¹¹ and at EniChem Corporation, Jen's group¹² have doped thermally stable NLO chromophores into polyimide systems with a significant increase in the stability of the second order effect because of the high T_g of polyimide. Those groups have contributed one way or the other on the temporal and thermal stability problem in the NLO system. However, in addition to the concern over thermal/temporal stability, chemical stability and optical loss are also potential problems that need to be

taken into account in order for organic polymeric NLO materials to be used in a practical device.¹³

Besides interest in possible applications, Second Harmonic Generation (SHG) has been demonstrated to be an effective probe for interfaces and surfaces.¹⁴ We have also demonstrated that SHG can be used as a technique for an *in-situ* probe to study chain motion in pure bulk polymers subjected to a high electric field.¹⁵

The works done in this thesis utilize two techniques to study organic polymeric nonlinear optical systems: namely, Mach-Zehnder interferometry and the Maker Fringe phase matching technique. Mach-Zehnder interferometry was used to characterize the electro-optical coefficients; the Maker Fringe technique is used to determine the second order susceptibility, $\chi^{(2)}$. Both Pockels coefficient, r , and the second order susceptibility, $\chi^{(2)}$, are related to the intrinsic molecular second order hyperpolarizability, β , the number density, the local field factor, electric field poling, and the manner in which dipoles oriented in the bulk. This thesis is mainly concerned with each of these elements will affect the magnitude of the bulk polarization. Our interest is to understand the poling/decay dynamics and its temperature dependence of NLO polymers.

In Chapter II, we demonstrate by using the chromophore concentration dependence to show that the free oriented gas model is not adequate to describe the order parameter. In the free oriented gas model, the intermolecular interaction is excluded. We show that the dipole-dipole interaction will enhance

the bulk polarizability as the chromophore concentration increases. Using the Maker fringe technique in the SHG measurement, we obtain a quantitative value of the orientational order parameter from $\chi^{(2)}$ value. In this chapter, we introduce equations necessary for the presentation of this work and those which are developed during the course of this work. A detailed theoretical correction theory related to the dipole correlation function based statistical mechanics has been developed by Wang.¹⁶

After incorporating of the dipole-dipole interaction and showing its effect on polar orientation order parameter (POP), we present in Chapter III experimental results on the temperature and poling field dependence of POP in guest/host NLO polymer systems. We have associated the time dependence of the POP with the orientational time correlation function. We investigate the shape of the orientational relaxation profile and deduce the mean relaxation time from the SHG intensity decay curve. We have found a lengthening “memory” effect on all polymer systems studied. We have also found a two step mechanism for the POP relaxation: (1) the fast relaxation process dominated by the surface charges, and (2) a slow decay, reflected by the dipole reorientation and the trapped charge hindrance effects. We find that at temperatures above T_g , the Vogel-Fulcher-Tammann equation describe well the dependence of the steady-state relaxation time on temperature dependence. Finally, we demonstrate that the order parameter relaxation curve observed from the absorption recovery experiment (a second order Legendre polynomial function)

has a much shorter relaxation time compared to the POP obtained from the SHG signal decay experiment.

In Chapter IV, we characterize the second-order susceptibilities for a novel main chain accordion polymer, which has the NLO chromophore covalently bonded head-to-head along the polymer backbone. This polymer has a high T_g and good thermal/temporal stability. However, the poling process induces degradation of this polymer. In the second part of Chapter IV, by monitoring the *in-situ* SHG signal from the pure blank polymers we are able to study the physics of polymer chain motion subject to a high electric field. This is the first to demonstrate SHG as a new technique for polymer physics research. Additional comparisons of the temperature dependent POP relaxation to the dielectric relaxation data are presented. With evidence from the inconsistency between birefringence and POP performance, and longer relaxation time for POP relaxation (compared to absorption recovering and dielectric relaxation), we conclude that SHG relaxation results complement that from absorption, refractive index, or dielectric loss measurements.

In the last chapter, we present electro-optical results on two guest/host polymer systems. By modulating the field at high frequency, we are able to eliminate signals from electrode attraction, electrostriction, thermal motion and piezoelectric effect. Non *e-o* contributions can also be reduced by replacing the sandwich configuration sample by an evaporated gold electrode sample. The quadratic *e-o* effect also contributes to the total signal and can be obtained

directly by measuring the modulated signal at the doubled frequency. POP's obtained from NLO chromophore concentration dependent $e-o$ coefficient measurements also suggest that the dipole-dipole interaction is important in the guest/host NLO polymer sample.

In the context of earlier pioneering research, and the on-going projects in our laboratory, this thesis has in part helped clarify some issues in the realm of organic polymeric NLO material research. As can be seen from this thesis, there are still many unanswered questions that need be addressed: Are the local field correction factors suitable for the solid polymer medium (especially in the resonance condition)? Is the second order hyperpolarizability, β , obtained from the solution environment comparable with that from the polymer matrix? What are the effects of trapped charges? Does the poling process change the polymer chain structure, and to what degree?

This is just the beginning of nonlinear optical research on organic polymeric systems; more sophisticated investigations of many interesting topics are going on every minute. We should expect many fruitful results and the commercialized implementations use organic polymeric based NLO devices in the near future.

References

- 1 . Zyss, J., *J. Mol. Electron.* **1985**, 1, 25.
- 2 . Walker, R. *IEEE J. Quant. Electron.* **1991**, 27, 654.
- 3 . Williams, D. J.(Ed), *Nonlinear Optical Properties of Organic and Polymeric Materials*, ACS symposium series 233, Washington, DC: American Chemical Society 1983.; Chemla, D. S., and. Zyss, J(Eds.), *Nonlinear Optical Properties of Organic Molecules and Crystals*, New York: Academic Press, 1987.; Marder, S. R., Shon, J. E., Stucky G.D.(Eds.), *Materials for Nonlinear Optics, Chemical Perspectives*, ACS symposium series 455, Washington, DC: American Chemical Society, 1991.; Prasad, P. N., Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers* New York: John Wiley & Sons 1991
- 4 . Katz. H. E., Schilling, M. L., Ungashe, S., Putvinski, T. M., Scheller, G., Chidsey, C. E. D., Wilson, W. L., *Proc. SPIE* **1991**, 1560, 370.
- 5 . Marks, T. J., in:" *Descriptive Chemistry of Self-Assembled Multilayer Second-Order NLO Materials: Chemical, Microstructural, and Performance Interrelationships*", Materials Research Society Fall Meeting, Boston MA, December, 1993.
- 6 . Ermer, S., Lytel, R. *Appl. Phys. Lett.* **1992**, 61,2272.
- 7 . Ferm, P., Knapp, C., Yardley, J., Hu, B., Zhang, Z., Auston D. *Appl. Phys. Lett.* **1991**, 59, 2651.; Girton, D., Kwiatkowski, S., Lipscomb, G., Lytel, R. *Appl. Phys. Lett.* **1991**, 58, 1730.; Teng, C. *Appl. Phys. Lett.* 1992, 60,

-
- 1538.; Lipscomb, G. F., Lytel, R. S., Ticknor, A. J., Van Eck, T. E., Girtton, D. G., Ermer., S. P., Valley, J. F., Kenny, J., Binkley. E. *Proc. SPIE* **1991**, 1560, 389.
- 8 . Takizawa, K., Kikuchi, H., Fujikake, H., Namikawa, Y., Tada, K. *Optical Engineering* **1993**, 31 (8), 1781-1791.
- 9 . Oprysko, M. *Proc. SPIE* **1990**, 1213, 76.
- 10 . Lindsay, G. A., Nee, S. F., Hoover, J. M., Stenger-Smith J. D., Henry, R. A., Kubin, R. F., Seltzer, M. D. *Proc. SPIE* **1991**, 1560, 433.
- 11 . Wu, J. W., Lytel, R. *Appl. Phys. Lett.* **1991**, 58, 225.
- 12 . Becker, M. W., Sapochak, L. S., Ghosen, R., Xu, C., Dalton, L. R., Shi, Y., Steier W. H., Jen, A. K.-Y. *Chem. Mater.* **1994**, 6, 34.
- 13 . Skumanich, A., Jurich, M., Swalen, J. *Appl. Phys. Lett.* **1993**, 62, 446.
- 14 . Shen, Y. R., *The Principle of Nonlinear Optics*, New York:: John Wiley & Sons, 1988, pp. 493-504.; Tom, H. W. K., Mate, C. M., Zhu, X. D., Crowell, J. E., Heinz, T. F., Somorjai, G. A., Shen, Y. R. *Phys. Rev. Lett.* **1984**, 52, 348.; Hunt, J. H., Guyot-Sionnest, P. Shen, Y. R. *Chem. Phys. Lett.* **1987**, 133, 189.; Harris, A. L., Chidsey, C. E., Levinos, N. J., Loiacono, D. N. *Chem. Phys. Lett.* **1987**, 141, 350.; Grubb, S. G., DeSantolo, A. M., Hall, R. B. *J. Phys. Chem.* **1988**, 92, 1419.; Shen, Y. R. *Nature*, **1989**, 337, 519,
- 15 . See Chapter IV in this thesis.
- 16 . Wang, C. H. *J. Chem. Phys.* **1993**, 98, 3457.

II. Dipolar Interaction Assisted Effects on Second Harmonic Generation*

A. Introduction

Organic molecules, with conjugated π -electron systems terminated by donor and acceptor groups, are known to exhibit large second order hyperpolarizabilities.¹ Polymer systems containing these molecules can be made to produce a large second order nonlinear optical (NLO) effect, such as second harmonic generation. The most common method employed to obtain a high second order NLO effect is to polarize the polymer system by applying a strong DC electric field, a process known as poling. To pole the system, the polymer containing the nonlinear optical molecules is first processed as a film; the film is heated above its glass transition temperature (T_g) in the presence of an electric field in order to orient the NLO chromophore; the polymer film is then cooled below T_g to lock the orientation in place before the field is removed. This process breaks down the isotropic symmetry of the amorphous polymer and freezes the electric dipoles in a noncentrosymmetric order.

The fundamental second order NLO effect in the polymer lies in the existence of the polar orientational order parameter (POP), induced by the external poling field E_p . When the POP vanishes, the second order NLO effect also vanishes. To maximize the NLO effect, it is important to understand the relationship between the poling process and the behavior of the POP. The effect of NLO chromophore concentration on the POP is also important, because it is associated with the interaction between the dipole moments of chromophores.

* The contents in this chapter were extracted from the paper published in *J. Chem. Phys.*, **1993**, *98*, 3463.