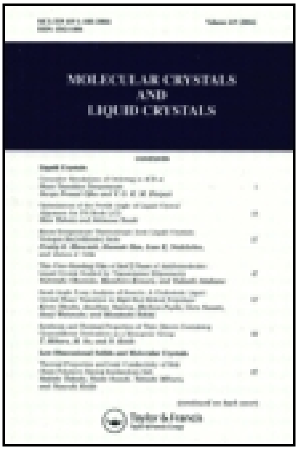

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Surface Oriented Polymers for Nonlinear Optics

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SURFACE ORIENTED POLYMERS FOR NONLINEAR OPTICS

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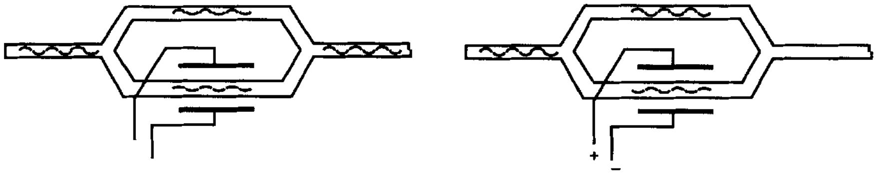
Abstract

A large number of criterion must be met for a material to be of practical value in the development of wave guide optical switches. We have taken the approach that optimal and permanent orientation is of prime importance. We have addressed the question of alignment by developing techniques for the polymerization of aminoacids to form vertically oriented helices on gold surfaces. Using this approach, we have been able to grow layers of alanine, methylalanine (ethylglycine), leucine, and phenylalanine on gold deposited on silicon that are 1-2000 Å thick. Further, grazing angle, FTIR measurement are consistent with the presence of only helical peptides for alanine and 90-95% helical forms of the peptides derive from the other aminoacids. These helical columns are oriented to a major extent vertically relative to the surface. The key feature that of the technique is the use of a base attachment for the gold surface that maps out the correct surface area corresponding to that required for the helices. Details of the synthesis and analysis of these polymer films will be described.

INTRODUCTION

Macroscopic engineering is an important requirement for use of organic polymers in high technology applications. In particular, optical switches based on second order, non-linear effects require materials with unidirectional alignment of molecular scale, strong dipole moments over domains that exceed the wavelength of light.[1-6] A range of techniques for alignment of dipoles have been investigated, including: single-crystal materials; liquid crystals; Langmuir-Blodgett films; poled polymers; and host-guest inclusion complexes.

Current technology for optical switching involves phase-shift wave guides with polymers doped with dipolar guests as well as polymers with appended, polar subunits. Orientation is achieved by electric field polling at elevated temperatures. This technique is limited, however, by the long term thermal instability, the limited degree of alignment achievable with non-arching potentials, and the degradation of optical properties that limits amounts the quantity of dipolar material that can be incorporated to relatively small.



ON state: light split between two identical paths - recombination results in no change and transmission of light.

OFF state: electric field applied to one branch of wave guide causes an increase (or decrease) of dipole moment. The resulting increase (decrease) in refractive index phase-shifts one path and effects net cancellation upon recombination.

FIGURE 1 Operation of a Phase Shift Optical Switch

We report here an entirely new method for achieving unidirectional alignment of rigid polymers in large assemblies.

BACKGROUND

Polymerization of organic monomers to form polymeric materials under normal circumstances results in a bulk sample with no net dipole moment, driven to this state by the entropy. Even relatively large, macroscopic applied fields do little to orient a bulk material. Experimental methods for measuring the degree of alignment accurately are not available but estimates place the "net" alignment at less than 10%. We felt that the strong influence of entropy in favoring a random orientation of materials could be circumvented by the simple expedient of growing polymer chains from the surface of suitably smooth materials. The unidirectionality inherent in a surface will thus be propagated at each stage of the operation to achieve a net orientation of the material. With a suitably rigid, individual structural units (to be discussed below), a macroscopically aligned material that is unidirectionally oriented from the surface can be built where the total negative entropy inherent in the macroscopic alignment can be accumulated in small steps as the materials grow. We believe that each of the fundamental scientific principles necessary for the success of this program are already in place. However, to our knowledge they have not been combined in the fashion just described to solve the problem of aligning polymers for optical switches.

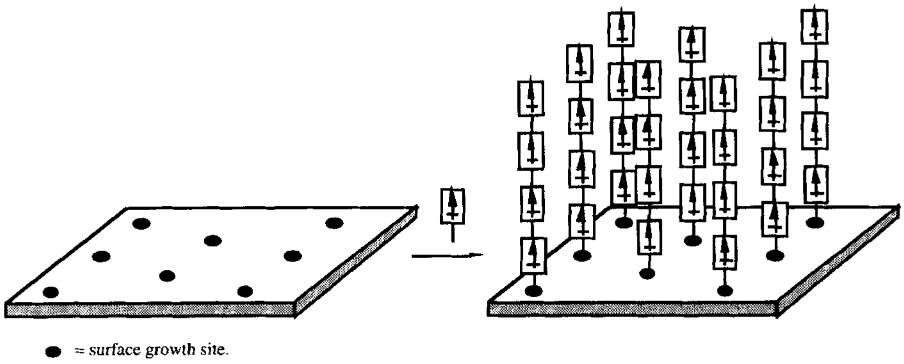


FIGURE 2 Growth of oriented layers on a smooth surface. The arrows represent dipole orientations with directionality imposed by the direction deposition of the monomeric units as they build away from the surface

Continuation of the unidirectionality of a surface can only be guaranteed if each chain will maintain a rigid, linear directionality. Without this feature, growth would be ordered near the surface but would become more random as the distance from the surface increased.

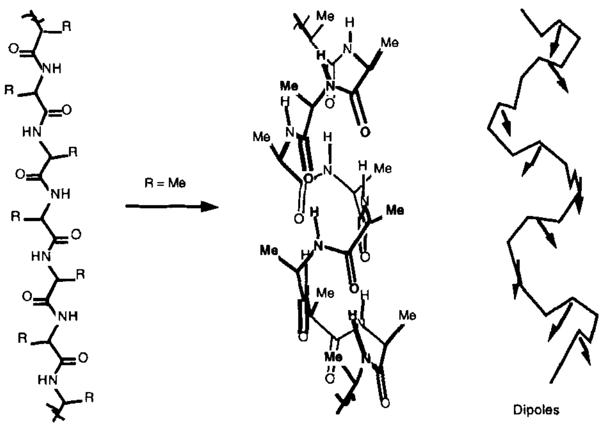


FIGURE 3 Peptide structural unit for surface growth.

The helical structure of α-amino acid-derived polyamides (peptides) is highly preferred with substituents other than hydrogen (e.g., methyl for polyalanine). Indeed, once approximately ten alanine units have been combined into an oligomer, the chain prefers a helix arrangement rather than alternate arrangements such as the β-sheet arrangement.[7] Further, the helix propagates more rapidly than does the β-sheet.[8] In the helix, the dipoles of the individual amide units pointing nearly parallel to the major axis of the chain and alternate, left to right, along the chain. The amide unit of polypeptides resemble the functionality in urea, which was the first substance (as a crystalline material) used to demonstrate second order non-linear properties expressed by generation of the second harmonic of laser light.

The selection of an appropriate surface is critical to the success of this program. Mallouk[9] has already demonstrated that very regular growth (albeit, in a stepwise fashion) is possible from the surface of a silicon wafer based on the pioneering work of Sagiv.[10] The multilayers that he has built are very regular and flat. For our purposes silicon will serve as an ideal substrate since it will permit integration of optical switching devices with electronic circuitry.

Well-defined layers of gold are formed on silicon surfaces when a thin, intervening layer of chromium is present. A number of organic materials can then be attached to the gold surface taking advantage of the affinity of thiol groups for this metal. Whitesides[11] has shown that organic materials can be deposited on the surface of gold when a thiol group is present, and that a regular and densely packed monolayer can be deposited in this fashion. These simple alkyl chains have interchain contact distances *smaller* than the interatomic distance of gold and therefore tilt on the surface. By contrast, the helix formed by polyalanine occupies considerably more space (diameter of encompassing cylinder ~8.8 Å) and these cylinders can "tight pack" on the surface with nearly vertical alignment (Figure 4). Close and regular packing of the polymer chains will be an important component of maintaining high optical transmission. From the point of view of practical application as wave guide material for optical switching, polypetides have the ideal characteristic molecular functionality of the peptide chain will be they are transparent to the fundamental (as well as second harmonic) of the infrared laser light to be switched.

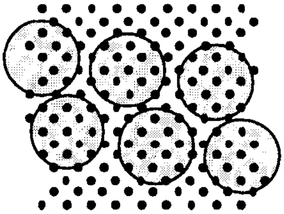


FIGURE 4 Vertical "Cylinders" of polypeptides on Gold, drawn to scale.

However, the difference between the space occupied by a helical peptide (-9 Å) and the interatomic spacing of gold (~4 Å) dictated that we anchor a "seeds" to the surface from which the polymer would grow separated from each other by the size required by the helical peptide. We have solved this problem with the trithiol **1** which adheres tightly to the surface of gold and maps out the required area.

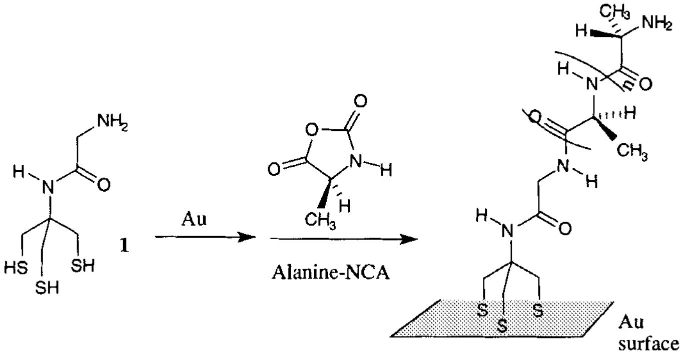


FIGURE 5 Aminotrithiol **1** adsorbed onto Au surface followed by formation of polyalanine using the N-carbonic anhydride of alanine.

Polymerization of the N-carbonic anhydride (NCA) of alanine takes place on this surface, forming a layer that has clean and very sharp adsorptions in the grazing angle, infrared spectrum for the amide I and amide II bands. The adsorption frequencies of these bands are fully consistent with essentially completely helical polymer. A spectra

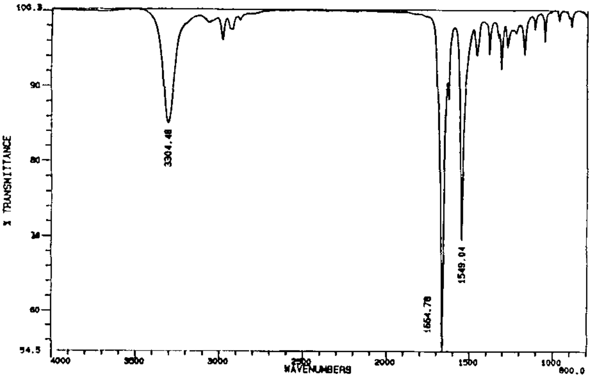


FIGURE 6 Helical polyalanine formed by polymerization of the N-carbonic anhydride starting with aminotrithiol 1 as seed on gold surface.

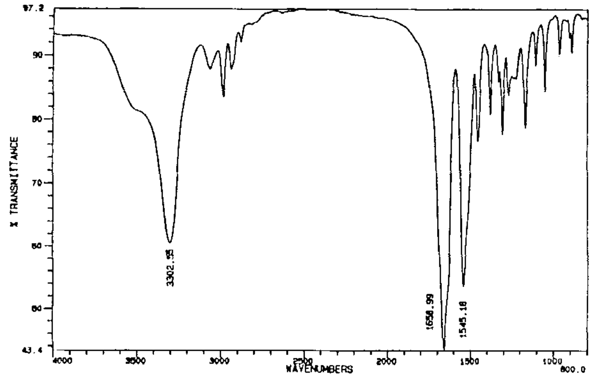


FIGURE 7 Polymer of alanine formed in solution at the same time that polymer was formed on amionotrithiol 1 on gold.

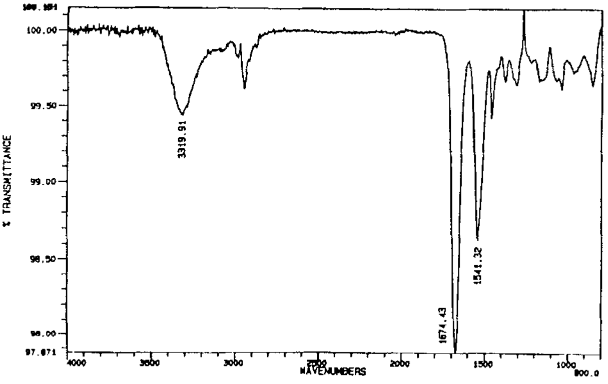


FIGURE 8 Polyalanine consisting of 24 units, on gold.

of polyalanine on gold is shown in Figure 6, contrasting with that of polyalanine formed simultaneously in solution (Figure 7) and a 24-mer of polyalanine on gold (Figure 8) generated by sequential addition of three-alanine subunits.

The thickness of these layers was measured by two techniques, elipsometry and atomic force "stepping" from bare gold to a layer of polymer. These results are in agreement within experimental error. Using infrared absorption to monitor thickness, we have determined that the rate of polymer growth is linear to thicknesses in excess of 2-3000 Å.

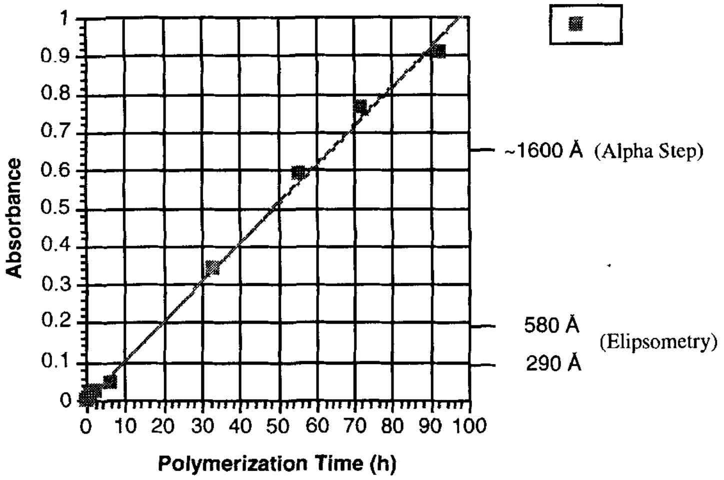


FIGURE 9 Growth rate of polyalanine formation on gold.

CONCLUSION

We have demonstrated an entirely new method for forming thick layers of ordered organic materials on surfaces. We envision many unique applications for these new materials and, as well, anticipate that the novel techniques that we have used for the production of ordered polypeptide layers will be applicable to other materials as well.

REFERENCES

1] D.S. Chemla and J. Zyss, Eds., Non-Linear Optical Properties of Organic Molecules and Crystals, Vol. 1 and 2, Academic Press, Inc., New York (1987).

2] D.J. Williams, ed. Non-Linear Optical Properties of Organic and Polymeric Materials, ACS Symposium Series 233, American Chemical Society, Washington, DC (1983).

3] G., Khanarian, Ed., Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications, Proceedings of SPIE-The International Society for Optical Engineering, Bellingham, WA (1986).

4] Organic and Polymeric Nonlinear Optical Materials - A Topical Workshop, sponsored by The Division of Polymer Chemistry, American Chemical Society, Virginia Beach, Virginia, May 16-19 (1988).

5] M.J. Bowden; S.R. Turner, Eds. Electronic and Photonic Applications of Polymers, ACS Advances in Chemistry Series 218, American Chemical Society, Washington, DC (1988).

6] D.J. Williams, Angew. Chem. Int. Ed. Engl. 23, 690 (1984).

7] Kricheldorf, H.R.; Mutter, M.; Maser, F.; Muller, D.; Forster, H. Biopolymers , 22, 1357-72 (1983).

8] Lundberg, R.D. and Doty, P. J. Amer. Chem. Soc. 79, 3961 (1957).

9] H. Lee; L.J. Kepley; H.-G. Hong; T.E. Mallouk, J. Am. Chem. Soc. 110, 618 (1988).

10] L. Netzer; J. Sagiv J. Am. Chem. Soc. 105, 674 (1983).

11] P.E. Laibinis and G. M. Whitesides, J. Am. Chem. Soc. 114, 1990 (1992) and references cited therein..