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Synthesis Of A Photoresponsive Polymer And Its Incorporation Into An Organic Superlattice

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Abstract

The synthesis of a photoswitchable polymer by grafting an azobenzene dye to methacrylate followed by polymerization is presented. The azobenzene dye undergoes a trans-cis photoisomerization that causes a persistent change in the refractive index of cast polymer films. This novel polymer was incorporated into superlattices prepared by spin casting and the optical activity of the polymer was maintained. A modified coextruder that allows the rapid production of soft matter superlattices was designed and fabricated.

Acknowledgment

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1. Introduction

Since the invention of the laser, the use of light in information technology has increased tremendously. However, of the three major components of information technology, namely signal transmission, storage, and manipulation, most progress has been made in the area of signal transmission by developing high quality optical materials such as doped silica and claddings for use in optical fibers (1). High speed all-optical computing has not been fully realized mainly because of the lack of materials with specific properties that allow for more sophisticated light storage and for manipulation of the amplitude, frequency, phase, or direction of light without having to either convert light into electrical signals or having to mechanically modify the signal.

Historically, two concepts in modern materials science have been particularly successful in generating new material properties. First, novel physical properties have been obtained by arranging nanometer thick semiconducting inorganic layers into superlattices. By stacking what are essentially 2D inorganic layers, interesting optical, electrical, and magnetic properties can be generated through band gap engineering, quantum confinement, and tailored coupling. An impressive application of this idea is the design, fabrication, and characterization of the quantum cascade laser at Bell Labs (2).

The second enabling concept in materials science is the realization that modern organic chemistry enables the physical and chemical properties of soft matter (polymers, oligomers, and organic molecules in general) to be manipulated much more easily than the properties of inorganic compounds. Soft matter is no longer thought of as a merely insulating, compliant material: chemists and materials scientists can now endow soft matter with electrical conductivity, optical activity, superconductivity, magnetism, and many other properties. In fact, this precise control of the properties of materials has sparked a huge worldwide race to fabricate efficient and inexpensive organic light emitting materials (3). By contrast, the chemical manipulations that can be carried out in solid state inorganic nanolayers are often limited by a variety of reasons including equilibrium thermodynamics and lattice matching considerations.

In this report we document our accomplishments combining these two approaches and create new materials that can be used to manipulate light. We investigate the application of organic synthesis to create polymeric materials that undergo a change in their refractive indexes when stimulated by an ultraviolet (UV) trigger signal. We also explore techniques to incorporate these polymeric materials into superlattices and thus create novel reflecting materials. Figure 1 summarizes our strategy.

A) Synthesis of novel polymer

Nanolayer a: novel polymer with index of refraction change triggered by UV light

Nanolayer b: Standard polymer material

B) Superlattice fabrication

Organic Superlattice: formed by stacking nanolayers a and b
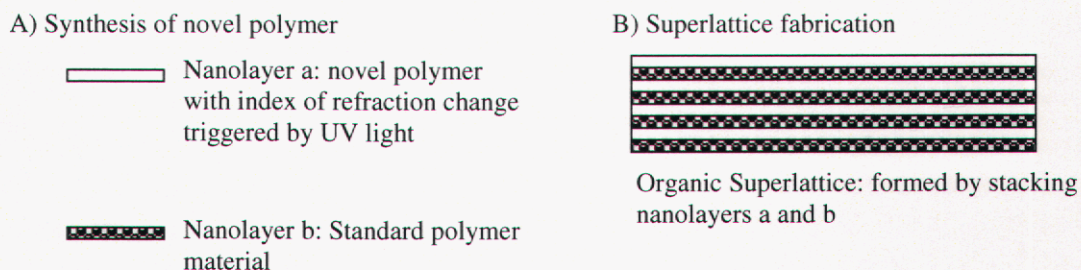
Figure 1: Schematic representation of our strategy for creating new optical materials. (a) a novel polymer that changes its index of refraction when triggered by a UV light signal is synthesized and then (b) combined with another polymer to form a superlattice.

Specifically, our strategy for creating new optical materials will build upon the work reported by Weber et al. (4) on birefringent polymer nanolayer superlattices with enhanced reflectivities. These superlattices consisted of alternating nanolayers of isotropic polymethyl methacrylate (PMMA) and either birefringent polyester or birefringent syndiotactic polystyrene. The reflectivities of the p- and s- polarized light from the superlattices is determined by the indexes of refraction, the thickness of the layers, and the angle of incidence. Thus, by combining nanolayers with different indexes of refraction, the value of the reflection coefficient at a specific angle at the nanolayer interfaces could be predictably controlled. By building nanolayers of specific thicknesses, the center wavelength and the bandwidth of a high reflectivity band versus the angle of incidence can be determined. However, as reported these superlattices are passive materials: once fabricated, the optical properties cannot be changed in response to the reflected light or to a trigger signal. Our strategy in this project is to modify and tailor, using organic chemistry, the composition of one of the nanolayers to include photoresponsive molecules that could change the indexes of refraction of that set of nanolayers when triggered by an external signal. This change in refractive indexes will change the overall reflectivity and the value of the Brewster angle thereby enabling optical switching.

2. Experimental

Synthesis of Photoresponsive polymers: Our synthetic efforts were
focused on grafting azobenzene dye (ABD) chromophores into methacrylate polymers .
As reported in the literature, ABD's change their conformation when irradiated with UV
light (5). ABD's exist as two isomers, a rod-like thermally stable trans isomer and a bent,
metastable cis isomer (6, 7). When the trans isomer is irradiated with light of the
appropriate wavelength it isomerizes to the cis-conformation (Fig. 2). When the light is
turned off, a fraction of the ABD's will retain the cis configuration. The cis-isomers
subsequently relax back into the trans isomer configuration. The differences in electronic
polarizability between the trans and the cis isomers mean that if the ABD chromophore is
grafted to a polymer, the electronic polarizability and thus also the refractive index of the
grafted polymer can be changed by irradiation with UV light (8).
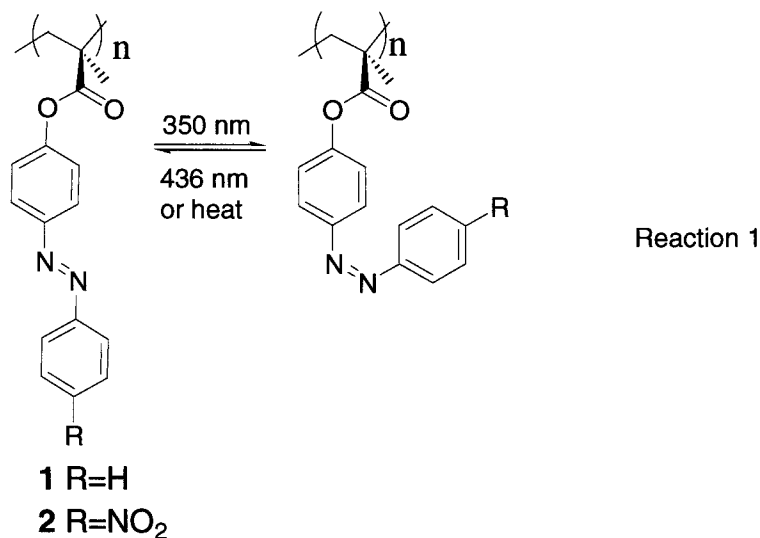
Figure 2. Expected photoinduced isomerization of ABD grafted onto PMMA .

Two types of ABD-grafted PMMA were initially prepared with different polar and
electronic substituents (Fig. 2). ABD-grafted polymer **1** contains no substituent in the
azobenzene para position while polymer **2** contains a para nitro group. Potentially, two
synthetic routes are possible to generate ABD-grafted PMMA. In approach PMMA is
first synthesized and then the ABD is grafted onto the polymer chains. In another
approach, ABD-grafted methylmethacrylate monomer units are first synthesized and then
polymerized in a subsequent step.

We generated ABD-grafted PMMA by first synthesizing grafted monomer units and thus
ensuring minimal steric effects on the final yield. **1** and **2** were respectively prepared by
reacting 2-methacryloyl chloride (**3**) with 4-(phenylazo)phenol (**4**) or 4-(4-
nitrophenylazo)phenol (**5**) in the presence of triethyl amine in THF (reaction 2) at room
temperature followed by AIBN catalyzed free radical polymerization (reaction 3) in

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refluxing THF. The final product was isolated by dripping the THF solution into cold petroleum ether. ABD-grafted PMMA **1** and **2** were obtained in yields of 85% and 15% respectively. Low yield of **2** was likely due to formation of insoluble high molecular weight precipitates.

As a control, a non-polymerizable azobenzene model compound (**9**) similar to monomer **6** was prepared. **9** was synthesized in 95% yield through reaction of 4-(phenylazo)phenol (**4**) with isobutyryl chloride (**8**) in the presence of triethyl amine in THF (reaction 4).

Reaction progress was monitored using ^{1}H-NMR and the optical activity of the ABD-grafted PMMA, MMA, and of model compound **9** was verified by collecting UV-vis absorbance spectra in solution. All compounds were initially prepared in approximately 5 g batches. Approximately 50 g batches of compound **1** was later prepared with no significant procedural modifications.

Reaction 2

3

4 R=H
5 R=NO$_2$

6 R=H
7 R=NO$_2$

Reaction 3

6 R=H
7 R=NO$_2$

1) Refluxed AIBN catalyzed polymerization
2) Cold pet ether

1 R=H
2 R=NO$_2$

Reaction 4

8 + **4**

THF
TEA
Room Temp

9
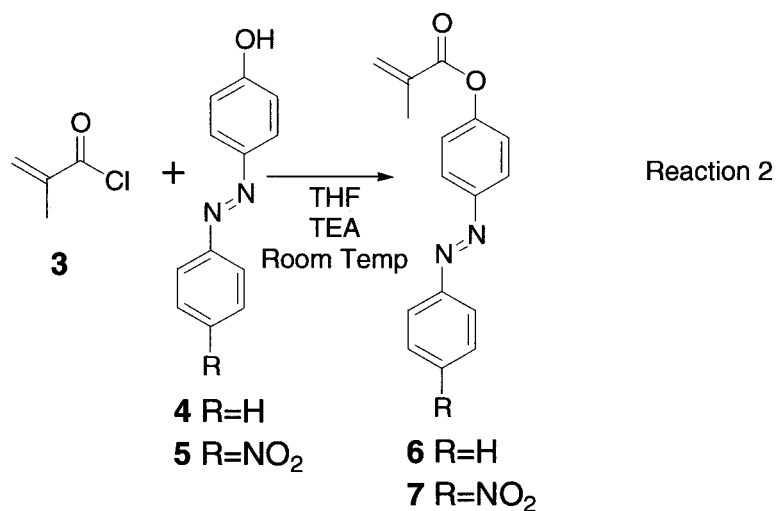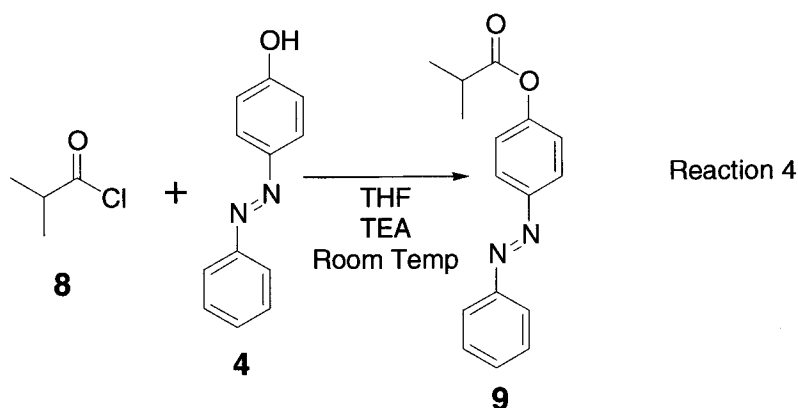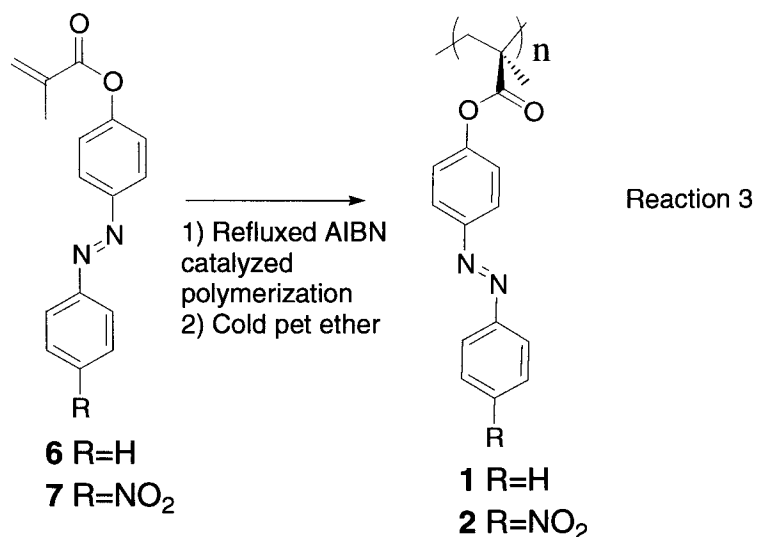
Synthetic Schemes: Organic synthesis reactions used to generate ABD-grafted compounds.

Physical characterization of ABD-grafted polymers:

The optical response of the ABD-grafted PMMA was verified by collecting UV-visible (UV-vis) absorbance spectra of methylene chloride solutions. Since the desired novel optical materials will be used in the solid state, the optical activity of the ABD-grafted PMMA was verified by taking UV-vis absorbance spectra of solid thin films spin cast onto quartz slides. The persistent change in the index of refraction for each grafted PMMA was quantified by taking ellipsometric readings on solid thin films spin cast onto silicon wafers. The thermal stability of the most promising polymer, **1**, was checked using thermal gravimetric analysis.

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Superlattice fabrication: Two routes were explored to fabricate organic superlattices: a modified spin casting procedure and multilayer coextrusion. Spin casting was selected as a relatively quick, low tech way to select the most promising photoresponsive polymer.

Modified spin casting procedure: Each layer that makes up the superlattice stack was spin cast, floated, and then collected as described below. The solvent used for spin casting was toluene. Given the lower volatility of toluene, it was found that a more uniform film could be obtained. However, these films are noticeably thinner than those spun with higher volatility solvents. This meant that a higher polymer concentration had to be used. Another reason for using toluene was that it was used previously in creating polystyrene films, and a concentration for a desired film thickness had been predetermined.

Two types of 8-layered stacks were fabricated. One type consisted of alternating layers of polystyrene and of injection molding grade PMMA. The other type consisted of alternating layers of polystyrene and injection molding grade PMMA mixed with **1**. The ratio of the PMMA to **1** was 2:1 respectively. All of the films were spun from a solution of 10% weight fraction in toluene (the solution for the PMMA/**1** film contained 0.333g of **1**, 0.666g of PMMA, and 90g of toluene). To prepare the toluene solutions, the polymers were stirred into the toluene and the container was then placed into a sonicator for approximately 2 hours and then placed into a 40 °C oven for a minimum of 24 hours. The solutions were then filtered through 5μm and 1μm diameter membranes.

The procedure for spin-coating was as follows: A glass slide was thoroughly washed with toluene and then dried with an inert gas (argon). The slide was then placed into an ozone cleaner for 5 minutes. The slide was put on the spin coater vacuum chuck and flooded with toluene. It was then spun at 1500 rpm for approximately 60 seconds until it was dry. Finally, the solution with the polymer was added to the slide by means of a glass pipette (which was cleaned with toluene prior to use) and the slide spun. The parameters for the spin coating steps were 1500 rpm for 120 seconds.

After the film was spun on the glass slide, a scalpel was used to scrape the sides of the slide so that the film would come off more easily. A large container to hold deionized (D.I.) water for floating the film off the glass slide was cleaned with toluene and dried with argon. The cleaning process was repeated for each film that was floated. Once the container was cleaned and filled with D.I. water, the glass slide was placed into the water at a shallow angle of attack. The film would separate from the slide and float to the free surface of the water. The floating released film was carefully scooped out onto a wafer holding the stack of previously produced films.

The initial film on each of the 8-layered samples was the polystyrene film (10% concentration). This initial film was spun directly onto a silicon wafer, not a glass slide. The second layer was the PMMA/**1** film. Each film thereafter alternates between the polystyrene and PMMA/**1** film. After a new layer was added, the wafer was air dried vertically to remove any trapped water.

Multilayer coextrusion: The purpose of multilayer coextrusion is to bring together two or more polymers into a superlattice structure with continuous layers of controlled thickness. Once the coextrusion system is set up, superlattice production will be fast and inexpensive. However, considerable time and resources must be invested to design, fabricate, and test the coextrusion system. The funding and time frame of this project only allowed for the design and fabrication of the coextrusion system. Figure 3 diagrams the coextrusion system built at Sandia. Details on the principles of coextrusion and on the design of the Sandia coextruder will be presented later.
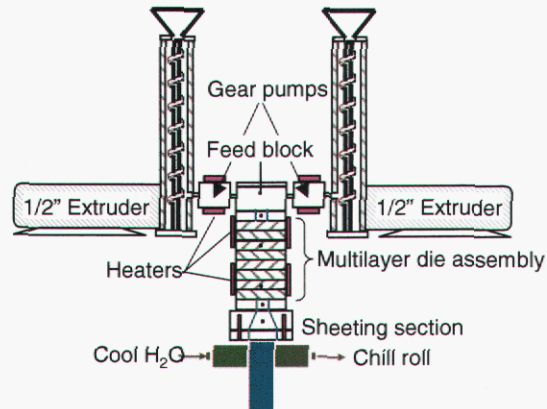
Figure 3. Diagram of coextrusion system.

3. Results and Discussion

Physical properties of ABD-grafted PMMA: All the ABD-grafted PMMA showed optical response in methylene chloride solutions (Fig. 4).

ABD-Grafted PMMA Exposed to 350 nm Light
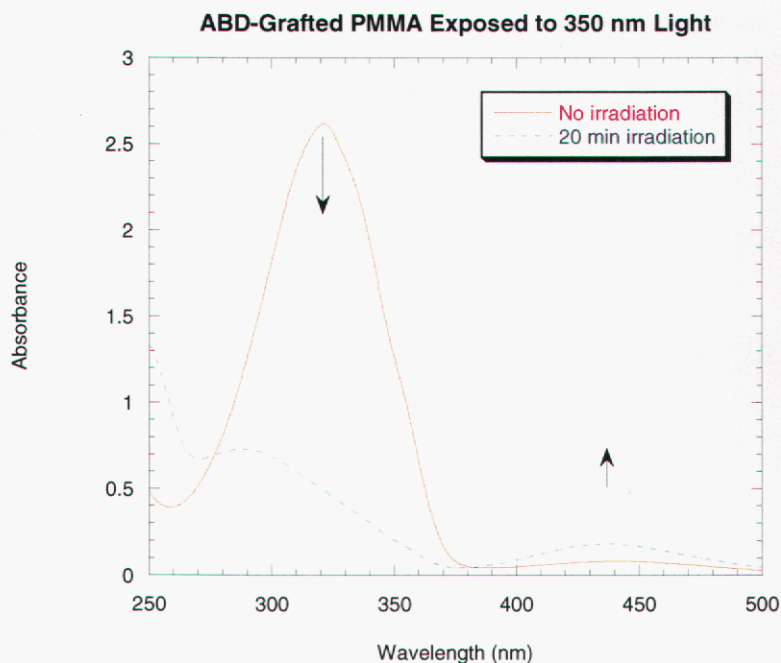
Figure 4: Absorbance spectra of **1** before and after irradiation with 350 nm light.

All the ABD-grafted polymers (**1**, **2**), the ABD-grafted MMA monomers (**6**, **7**), and the saturated ABD-grafted model compound (**9**) exhibited an absorbance peak centered at 320 nm corresponding to the trans configuration and an absorbance peak centered at 436 nm corresponding to the cis configuration (the absorbance peak below 250 nm is due to the aromatic rings) (5-7). Irradiation with 350 nm light resulted in a decrease in absorbance at 320 nm and an increase in absorbance at 436 nm indicating formation of the cis isomer.

Thin films of all the synthesized compounds also showed the expected photochemical behavior. For example, irradiation of a film of compound **1** with 350 nm light over time resulted in a decrease in absorption at 320 nm and an increase in absorption at 436 nm, again indicating formation of the cis isomer (Fig. 5a). After 15 minutes of irradiation, a photostationary state was reached and no further changes in absorption were observed. The lower relative change in absorption at 436 nm is due to the cis isomer having a lower extinction coefficient than the trans isomer at 320 nm. Exposure of the film to a visible lamp resulted in complete isomerization back to the trans form within 2.5 hours (Fig. 5b). The same transformation occurred within minutes when the cis film was exposed to sunlight. The thermal isomerization from cis to trans was also monitored in the dark at room temperature and the first order rate constant of 4.6×10^{-6} s^{-1} was obtained. This rate constant is consistent with other ABD-grafted polymers reported in the literature (9).

(A)

(B)
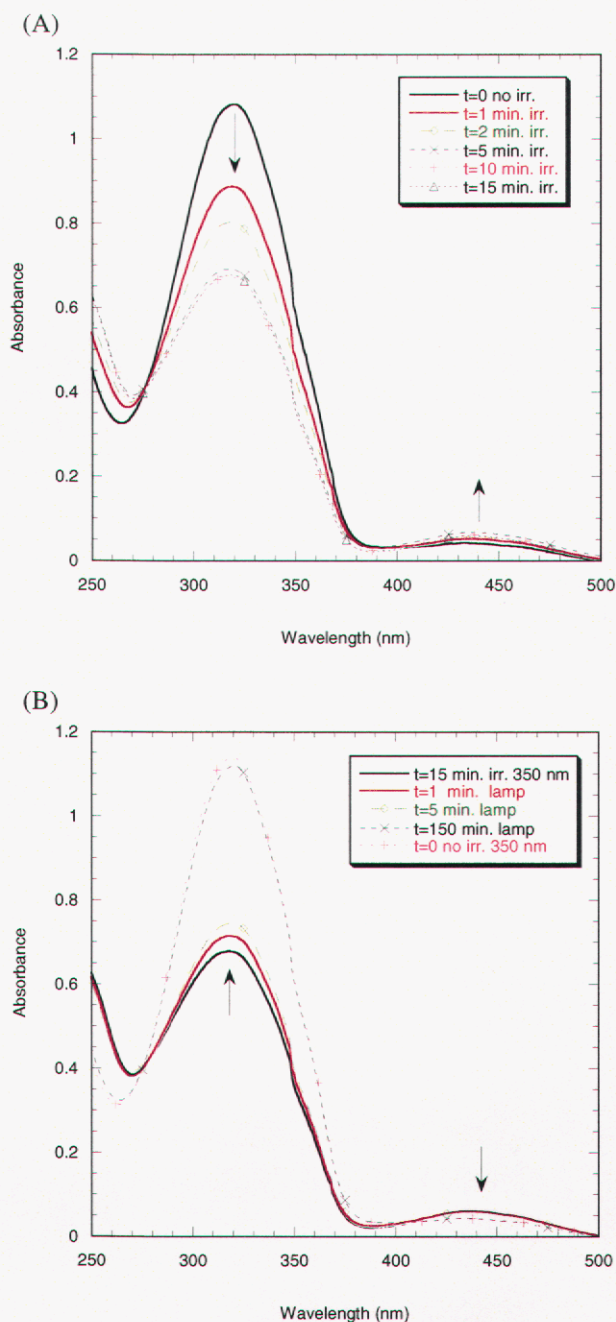
Figure 5: (A) Trans to cis isomerization of a film of ABD-grafted PMMA **1** and, (B) cis to trans isomerization of **1** with visible light.

Ellipsometric measurements (633 nm probe light at a 70° incidence angle) of the persistent change in the indexes of refraction after irradiating the samples with 350 nm light were carried out on films spun from methylene chloride solutions of 75% PMMA/25%ABD-grafted compound. The films were deposited onto silicon wafers

whose ellipsometric constants where measured a priori and accounted for. Figure 6 summarizes the observed index changes.

75% PMMA/25% ABD-Grafted Compound w/w
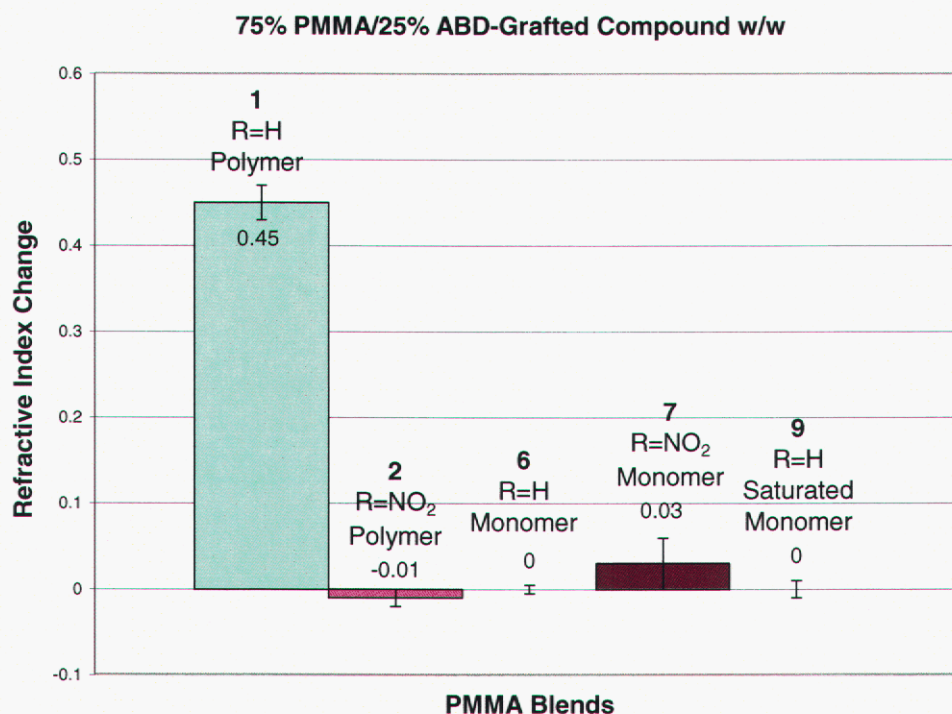
Figure 6: Refractive index change for thin films of ABD-grafted compounds. The refractive index change is plotted in absolute refractive index units with zero meaning no change in the refractive index after irradiation with 350 nm light.

Although all the ABD-grafted molecules showed an optical response in the solid state absorbance measurements, only **1** showed a useful persistent change in refractive index. **1** had on the average a refractive index change of 0.45, changing from $\eta = 2.85$ before irradiation to $\eta = 3.30$ after irradiation. After irradiation with 350 nm light, **1** was stored in the dark overnight at room temperature and its refractive index value returned to the value measured before irradiation. We believe that there is an opportunity for future research investigating the fundamental physical mechanisms behind this interesting optical behavior.

Another important property for the eventual incorporation of **1** into a coextruded superlattice is its thermal stability. Coextrusion can potentially expose the extruded polymer to temperatures as high as 230 °C for less than a minute in a nitrogen atmosphere. In order to test for thermal and oxidative robustness, compound **1** was heated at a rate of 1 °C/min in air in a thermal gravimetric analysis instrument. As seen in Figure 7, the compound exhibited negligible mass change below 250 °C and the same photoinduced refractive index change was measured in film samples after heating to 230 °C.
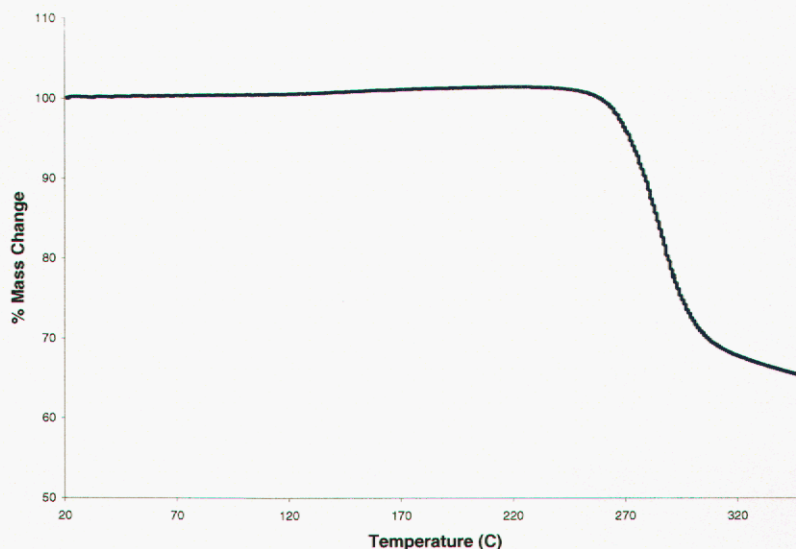
Figure 7: Thermal gravimetric analysis of compound **1** taken at a heating rate of 1°C/min in air.

Incorporation of ABD-Grafted PMMA Into Superlattice:

After determining that compound **1** had a large photoinduced index of refraction change in the solid state and that it had enough thermal stability for incorporation into extruded superlattices, a large 50 g batch of the compound was synthesized for eventual use in the coextrusion system. We also demonstrated the incorporation of **1** into a superlattice fabricated via the modified spin casting procedure (Figure 8).
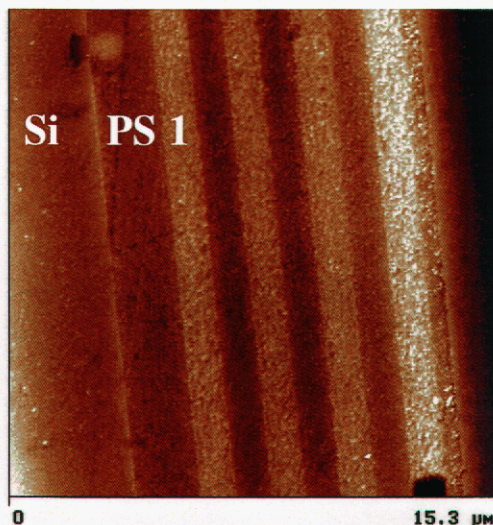
Figure 8: Atomic force microscopy cross-sectional scan of spun cast superlattice. Si: silicon substrate; PS: polystyrene layer; **1**: ABD-grafted PMMA compound **1**.

The layers fabricated by the modified spin casting procedure were approximately $1\mu m$ in thickness. Both a spin cast control superlattice containing polystyrene and pure PMMA and a spin cast superlattice containing polystyrene and 2:1 PMMA:compound **1** were heated to 200 C for 2 minutes and the refractive indexes measured with an ellipsometer (633 nm probe light at a 70° incidence angle) before and after irradiation with 350 nm light. The control superlattice maintained its layer structured after heating but as expected showed no change in its refractive index when exposed to 350 nm light. The superlattice containing **1** also maintained its layer structured after heating and it showed a refractive index change of 0.15, changing from $\eta = 2.1$ before irradiation to $\eta = 2.25$ after irradiation. We hypothesize that the measured refractive index change of **1** in a superlattice configuration differs from the refractive index change measured on a thin film because of the optical contributions of underlying polystyrene layers in the superlattice. After irradiation with 350 nm light, the spin cast superlattice containing **1** was stored in the dark overnight at room temperature and its refractive index value returned to the value measured before irradiation. Thus, we have shown that compound **1** is thermally stable, can form thermally stable superlattices in combination with polystyrene, and has a reversible change in its refractive index that can be triggered by irradiation with UV light.

Progress in Multilayer Coextrusion: Figure 9 shows the configuration of the multilayer coextruder built as part of this project.

Figure 9: Sandia's multilayer coextrusion system.

In multilayer coextrusion, a different polymer is fed into each extruder, which melts and pressurizes the polymer for further processing. The output of each extruder enters a gear pump. The gear pumps are critical to multilayer fabrication for two reasons. First, as the flight of the extruder screw passes the extruder outlet it creates a pressure pulse in the molten polymer stream. During layer multiplication a pressure pulse can lead to instabilities in the flow field and a break-up of the layered structure. The gear pump isolates the pressure pulse, removing a significant source of flow instability. Second,

there is a combination of drag and pressure-driven flow within the extruder. Thus, for a given extruder screw rotation rate, the output of molten polymer will depend on the viscoelastic properties of each polymer. The implication is that to match the thickness of each layer of the two polymer streams, the flow rate must be calibrated for each polymer under the extrusion conditions. The intermeshing teeth of the gears within the gear pumps have a fixed volume. Therefore, the gear pumps deliver a precise volume of molten polymer, independent of the polymer properties.

The formation of the multilayered structure begins by bringing the output of the two gear pumps together in a feedblock. As shown in Figure 10, this creates a bilayer that is "multiplied" to achieve a many-layered product. The multiplication method is simple, and was patented by Dow Chemical in 1969 (10). In the 1990's the technology was licensed to the 3M Company, primarily finding use as reflective materials in light pipes. In each multiplication element the flow is cut by a vertical piece in the flow field. The left half of the molten stream is sent through a channel to the lower portion of the multiplication element and spread back to the full channel width. Similarly, the right half is sent to the upper portion of the element and re-spread, such that at the end of the multiplication element the number of layers has doubled. Stacking these multipliers together causes the number of layers to increase as 2^{n+1}, in which n is the number of multiplication elements.

Polymer B

Polymer A

4 layers

8 layers

16 layers

$N = 2^{n+1}$
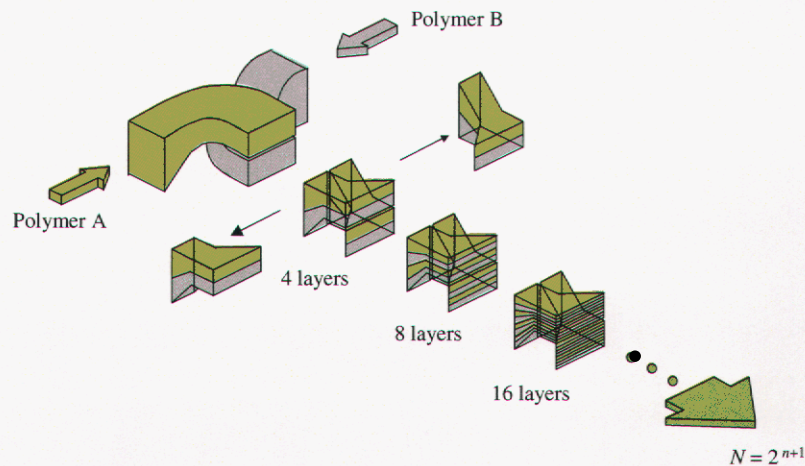
Figure 10: Schematic representation of multilayer creation via coextrusion.

After the desired number of multiplication elements, a sheeting section is placed in the flow field. The sheeting section is designed to vertically compress and horizontally stretch the multilayered structure to produce a sheet or film. The molten film exits the multilayer coextrusion line and enters a chill roll take-up device. The water-cooled steel rollers freeze the multilayered structure, preventing it from deforming.

There are many advantages to producing multilayered structures using this method. First, the polymers need only be melt-processable (i.e. dissolution in solvent is not required). Second, the film can be produced in near-infinite length, provided polymer is fed to the

extruders. Third, the thickness of the film is determined by the thickness of the sheeting die exit and the take-up speed, while the film thickness and the number of multipliers control the thickness of each layer. Thus, ten multipliers and a sheeting die with an exit thickness of 1 mm produce a film with each layer approximately 0.4 microns thick. Fourth, the layers do not mix significantly, due to the high viscosity of the polymers and the low flow rates. For example, estimating the Reynolds number using typical coextrusion parameters (melt viscosity of 1000 Pa-s, density of 1000 kg/m^3, flow rate of $1x10^{-6}$ m^3/s, channel diameter of 0.125 m) gives $1x10^{-5}$, which is orders of magnitude below the laminar-to-turbulent flow transition. Thus, structures such as those shown in Figure 11a (32-layer sample of polystyrene alternating with polypropylene, produced at the University of Minnesota) or Figure 11b (2000-layer sample of polycarbonate alternating with poly(methyl methacrylate) produced at the Dow Chemical Company) can be produced. Figure 11a is an optical image, in which each layer is approximately 25 microns thick. The AFM image in Figure 11b shows layers with a thickness of approximately 200 nm, which produce a final layered structure with mirror-like properties.

(A)   (B)
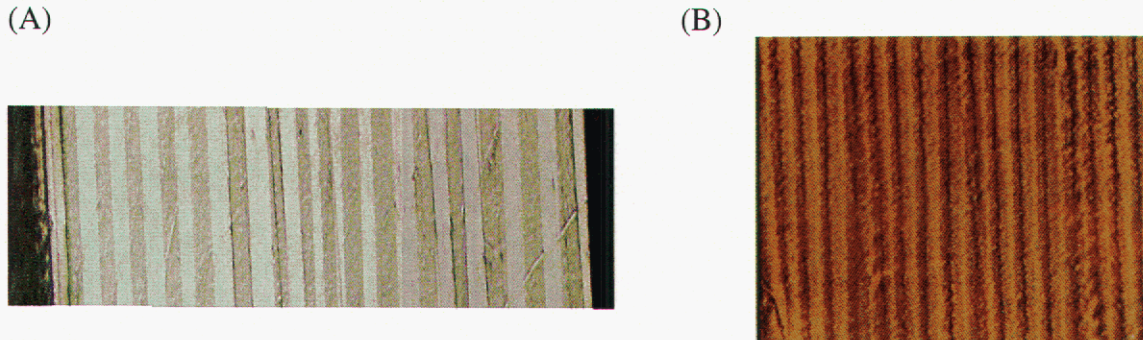
Figure 11: (A) 32 layers of polystyrene and polypropylene. (B) Section of a 2000-layer polycarbonate – poly(methyl methacrylate) sample.

We have modified the generalized multilayer coextrusion process to meet the requirements of this project and to improve the performance of the process. The common feed screw in each extruder has been replaced with a modified mixing screw. In addition to providing the shear flow and pressure necessary to melt and extrude the polymer, these modified screws have elements that produce extensional flow and should lead to enhanced mixing. This is critical if we are to blend polymers synthesized at Sandia California with other commercial materials.

Additionally, the multiplication process has been altered. Inhomogeneities in the velocity profile are produced in each multiplication element. If the multiplication elements are stacked sequentially, the vertical cut of the layered sample will transect an inhomogeneous flow. This leads to large variations in the thickness of each layer. Two modifications were made to the design that are expected to significantly reduce this effect. First, an open channel is added after each multiplier to re-equilibrate the velocity profile. Second, the orientation of the multipliers is reversed after each multiplication. The multiplication shown in Figure 10 has a clockwise orientation. We have placed a

multiplier with a counterclockwise (right section flows down, left section flows up) orientation after to further balance the polymer flow field.

Lastly, each multiplication increases the instabilities in the flow field and the likelihood that the layers will either break-up or have non-uniform thickness. Increasing the number of layers produced in the feedblock can reduce the number of layer multiplications required. The Sandia feedblock has been designed to separate the incoming extruder flow into four layers. Thus, eight total layers exit the feedblock. Since the flow division is accomplished before the layered structure is produced, we expect that there will be no negative impact on the layer uniformity or flow homogeneity.

The Sandia coextruder system was assembled at the end of this project. Additional funding from other sources will be needed to demonstrate and optimize the coextrusion of superlattices and to measure the optical performance of such materials. We expect the new coextrusion system along with polymer 1 to be the starting point for the synthesis of novel optical materials that will ultimately result in new optical devices and applications.

4. Conclusions

We have successfully synthesized a photoresponsive polymer by grafting an azobenzene dye to MMA followed by polymerization. The azobenzene dye undergoes a trans-cis photoisomerization that causes a persistent change in the refractive index of cast polymer films. This novel polymer was incorporated into superlattices prepared by spin casting and the optical activity of the polymer was maintained. A modified coextruder that allows the rapid production of soft matter superlattices was designed and fabricated.

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