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学位論文題目	Photoinduced Structural Changes in Photocrosslinkable Azobenzene-containing Polymers and Their Optical Applications (光架橋性アゾベンゼンポリマーの光誘起構造変化と光学応用に関する研究)
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論文内容要旨

This research involves photoinduced structural changes in crosslinkable azobenzene-based polymers and their applications to novel optical devices. The first emphasis of this study is to quantify the influence of crosslinking on photoinduced structural changes, especially at molecular and macroscopic levels. Immobilization of photoinduced macroscopic motions by photocrosslinking, which is the first research done in this area, is beneficial for industrial use as grating devices. The demonstration of novel optical devices using this technique is the second emphasis of this research. The conclusions in each chapter of this thesis are summarized below.

Chapter 1 describes the background for this study. Photoisomerization of azobenzene is the most important basic effect in this study. All of the photoinduced structural changes studied here are based on photoisomerization of azo chromophores. These photoinduced motions are classified into three levels - molecular, domain and macroscopic motions - and the present knowledge found in the literature was reviewed. In particular, photoinduced orientation and surface relief gratings, as molecular and macroscopic structural changes respectively, were explained in detail. In the last section of this chapter, the scope and the outline of this study were summarized. My aim was to clarify the influence of crosslinking on photoinduced structural changes and propose novel optical devices by combining photoinduced motions with photocrosslinking.

Chapter 2 presents the detailed preparation of a series of push-pull type azobenzene-containing polymers with crosslinkable groups used for this study. To compare positional relationship between azo chromophore and crosslinkable group, two different type copolymers, which contain azobenzene and acrylic groups 1) in the different side chains and 2) in the same side chains, were prepared through radical copolymerization. I fabricated typical copolymers that contain each

group either in the different side chain or in the same side chain as shown in Figure 1. All of the prepared copolymers were amorphous and their glass transition temperatures (T_g s) were over 80 °C. Crosslink density was easily controlled by changing comonomer ratios in the copolymers.

Chapter 3 focuses on photo crosslinking methods: by irradiating either a UV light or a 655 nm laser onto the crosslinkable azobenzene-containing polymers. Photo crosslinking reaction of the acrylic

groups was observed by monitoring the decay of the acrylic peak on IR spectra. Photocrosslinking with UV irradiation at 80 °C under nitrogen was accompanied by photo-degradation of the azo chromophores while 655 nm irradiation revealed photocrosslinking without any photo-degradation of the azo chromophores. The photocrosslinking proceeded at lower temperature and shorter polymerization time than thermal crosslinking. It was concluded that photocrosslinking using 655 nm laser was especially advantageous for the optical device fabrication using various photo-functionalities of azo chromophores.

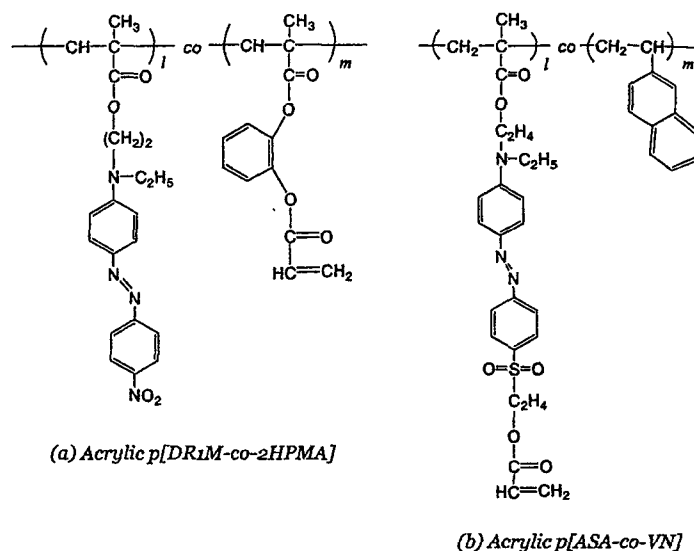


Figure 1. Copolymers containing azo chromophore and acrylic groups (a) in the different side chain and (b) in the same side chain. Copolymer ratio: $l/m=0.5/0.5$ by mol.

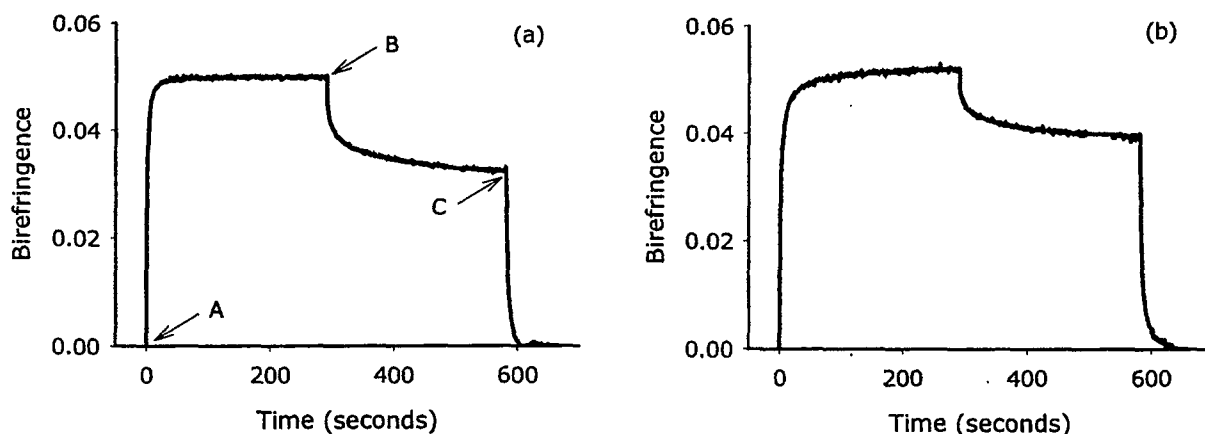


Figure 2. Birefringence behavior of copolymer, acrylic p[DR1M-co-HEMA] (DR1M content; 50 mol%) before (a) and after (b) crosslinking. At point A, a linearly polarized laser (writing beam) is turned on; at point B, the laser is turned off; and at point C, a circularly polarized laser (erasing beam) is turned on. Operating temperature; 25 °C.

This chapter also describes the influence of crosslinking on molecular level photoinduced structural changes. Photoinduced orientation behavior in the crosslinked network was measured by monitoring as birefringence of the azo chromophore (Figure 2). It was shown that photoinduced structural motions at molecular level were significantly affected by crosslinking. The stability of the photoinduced orientation was especially improved. This was more apparent with an increase in either crosslink density in the polymers or operating temperatures. The orientation behavior that was analyzed by biexponential curve fitting indicated that the movements of the azo chromophores were restrained by the crosslinked network. However, the azo chromophore was still mobile in the crosslinked network. Introduction of crosslinking into azobenzene-based polymers was expected to improve stability of reversible optical storages.

Chapter 4 explains photo-immobilization of photoinduced structural changes of the azo chromophores in the copolymers. In fact, the photoinduced orientation was not permanently locked even though photocrosslinking was performed simultaneously during photo-orientation. This observation is true even for the copolymer containing both azo moiety and acrylic groups in the same side chain. Investigation in the more tightly crosslinked network should be pursued to clarify the immobilization of structural change at molecular level by crosslinking.

On the other hand, relief gratings photo-inscribed on the polymer surface were immobilized by photocrosslinking. The photo-immobilized gratings were stable even at temperatures higher than the T_g ($=150\text{ }^\circ\text{C}$) of the crosslinked polymer whereas most of the gratings without crosslinking disappeared around its T_g ($=120\text{ }^\circ\text{C}$) (Figure 3). It was concluded that macroscopic structural changes such as polymer chain migration could be locked permanently by photocrosslinking. This advantage is expected to be used to improve the stability of optical grating devices.

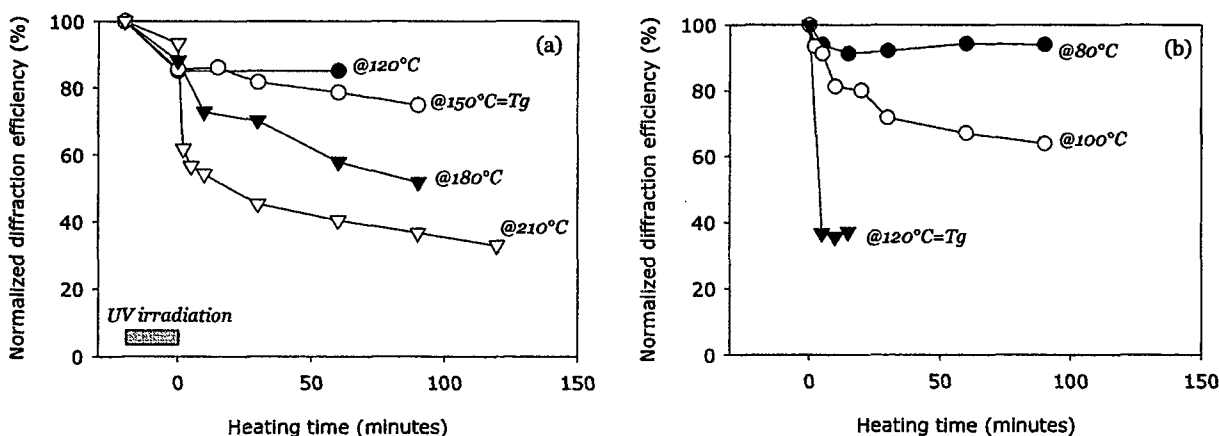


Figure 3. Thermal stabilities of normalized diffraction efficiency for grating films (a) photocrosslinked after grating inscription and (b) without crosslinking. T_g s of the photocrosslinked and non-crosslinked copolymers are 152 and 115 $^\circ\text{C}$, respectively. Copolymer sample: acrylic *p*[DR1M-co-HPMA].

Chapter 5 proposes novel optical devices using all optical processes by combining photoinduced molecular and macroscopic structural changes derived from photoisomerization of azobenzene with photocrosslinking. These optical devices were successfully fabricated and their optical characteristics were demonstrated. The possibility of polymeric EO switching by both the gratings and poled orientation was proposed and, it was shown that the output signals were modulated with the switching voltage at the frequency of 10 kHz. The optical losses at 824, 1,316 and 1,553 nm were measured on the slab waveguides including the azobenzene-containing polymer as a core and were less than 3.2 dB/cm after photocrosslinking. By taking advantage of both photo crosslinking and grating inscription techniques, waveguide wavelength filters with gratings were fabricated and showed a reflection peak at 1,310 nm (Figure 4). It is worth emphasizing that the grating waveguide device fabricated using all optical processes was able to filter a specific wavelength.

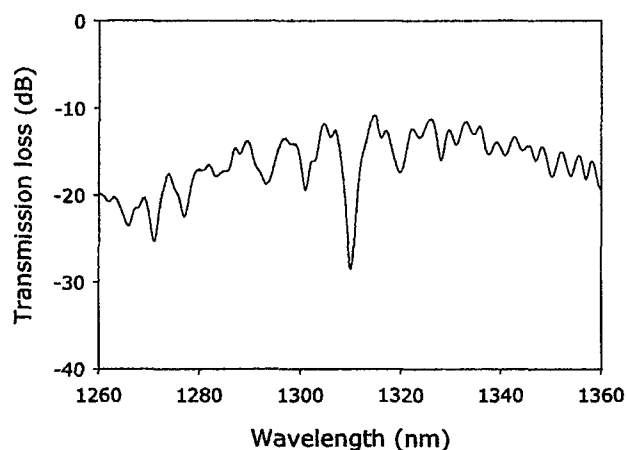


Figure 4. Transmission spectrum of a 10 μm wide wavelength filter with 5 mm long grating length. Waveguide length: 8 mm.

Chapter 6 describes a summary of the research presented here.

論文審査結果の要旨

本論文は、架橋性アゾベンゼンポリマーの光で誘起される構造変化とそれを応用して作製された光素子に関する研究であり、光誘起の構造変化への架橋の影響を、分子レベル、あるいは巨視的レベルで明らかにしたものである。

第1章では、序論として光誘起構造変化のドライビングフォースとなるアゾベンゼンの光異性化、およびそれによって誘起される構造変化に関して、既往の研究を中心にまとめ、本研究を概説している。

第2章では、本研究で使用した一連のプッシュ/プルタイプの光架橋性アゾベンゼンポリマーの調製法、およびその特性評価について記述している。架橋部位とアゾベンゼン部位の位置関係の異なる二種のポリマー、異なるポリマー側鎖にあるものと同一側鎖にあるものを設計、合成している。

第3章では、光照射による架橋形成を検討、紫外線照射により架橋が形成できることを明らかにしている。また、655 nmレーザー照射では、光分解することなく架橋が形成できることを見出している。構造変化として光配向挙動に着目した結果、架橋は光配向の緩和を著しく抑制できることを明らかにし、光配向を利用した光記録において記録の安定性向上につながることを明らかにしている。

第4章では、分子レベルの構造変化の固定化として、アゾベンゼン部位を光配向させながら架橋形成を行っている。巨視的な光誘起構造変化のひとつである表面グレーティングに光架橋を施すことで、形状を固定化できることを明らかにしている。マトリックスポリマーのガラス転移温度以上に加熱しても保持されることから、ホログラム記録などの熱安定性向上に寄与できる手法として提案している。

第5章では、分子レベル、巨視的レベルの両レベルでの構造変化と光による架橋形成を融合させることで、新規な光素子を構築、提案している。グレーティングとポーリング配向を利用した電気光学スイッチでは、10 kHzの変調電圧での応答動作を確認している。グレーティングと光架橋によるコアパターン形成による導波路型波長フィルターでは、特定波長の光を反射させることを検証するに至っている。

第6章では以上を総括し、架橋性アゾベンゼンポリマーの光で誘起される構造変化の活用方法を確立し、高分子光素子作製の可能性を明らかにしたものである。

以上要するに本論文は、架橋性アゾベンゼンポリマーの光で誘起される構造変化により光素子を実現したものであり、従来にない光プロセスによる高分子光素子作製の可能性を明らかにしたもので、材料化学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。