J. of the Chosun Natural Science
Vol. 6, No. 1 (2013) pp. 1 – 7

# Polymerization and Optical Properties of Polymers with High Tensile Strength Added Isocyanate Group

**A-Young Sung[1†] and Ki-Hun Ye[2]**

Abstract

Polyurethane resin containing isocyanate is marked by excellent tensile and mechanical strengths and this test aims to gauge its applicability as a medical high polymer. Tris [2-(acryloyloxy)ethyl]isocyanurate and hexamethylenediisocyanate were added to a basic mixing ratio of HEMA (2-hydroxyethyl methacrylate), MMA (methyl methacrylate), NVP (n-vinyl-2-pyrrolidone) and crosslink agent, EGDMA (ethylene glycol dimethacrylate) with increasing proportions and copolymerized respectively. Also, the basic physical properties of the polymerized high polymers including refraction rate, tensile strength, light transmission and water content were measured to confirm that they are appropriate as hydrogelcontact lenses. After measuring the physical properties of high performance polymers produced by adding tris [2-(acryloyloxy) ethyl]isocyanurate, it was found that the average tensile strengths of sample TRIS1 to TRIS10 were between 0.285 and 0.612 kgf, while the average values of refractive index were ranged from 1.441 to 1.449 with water content from 30.00 to 37.35%.The measurement of physical properties of the copolymers generated by adding hexamethylenediisocyanate showed that the average tensile strength of sample HEXA1 to HEXA10 ranged from 0.267 to 1.742 kgf, the refractive index ranged from 1.443 to 1.475 and water contents were in the range of 21.22 to 35.58%. In all combinations the transmission rates satisfied the transmittance of general hydrogel contact lenses. From theresults, it is possible to conclude that the produced copolymers can be used as contact lens materials with excellent tensile strength.

**Key words**: Polyurethane Resin, Polymer, Medical, Tris [2-(acryloyloxy) ethyl] Isocyanurate, Isocyanate Group.

## 1. Introduction

Polyurethane resin that contains isocyanate has been manufactured since the 1950s and it is the product of a polymerization reaction of glycol that has more than two functional groups of hydroxyls and over two diisocyanate and has -NH-COO- combination. In addition, while polyurethane is intrinsically thermoplastic, it turns into thermosetting one via three-dimensional transformation. The key properties of polyurethane form lies in that it has high tensile and mechanical strength, is heat-resistant, hot water resistant, coloring, weather-resistant, and water-resistant so that it is widely applied to a range of industries including rubber elastomers, painting, adherents, and artificial leathers, etc. In this study, functional high performance polymers by applying isocyanate containing tris [2-(acryloyloxy)ethyl]isocyanurate and hexamethylenediisocyanate to hydrogel contact lens materials were manufactured. Compared with glasses, contact lenses have clear advantages such as a wider area of vision and fewer changes in the retina. However, they also have some shortcomings in that they can cause a lot of ophthalmological problems as they directly contact eyes[1-3]. To facilitate oxygen provision to the cornea, it is required to have oxygen transmissibility[4-7]. Also, as eyes demand appropriate temperature and humidity and are directly exposed to air, it is more prone to be accessed by germs, subsequently more exposed to eye diseases. Therefore, the recent studies tend to focus on functional contact lens materials including antibiotic and UV-blocking functions to reduce optical functional disorders such as cataracts by blocking UV. The tensile strength related to elasticity and tensile destructive poweris a very important test that assesses the durability of materials among physical properties of contact lenses[8-11]. Tensile strength is most

[1]Department of Ophthalmic Optics, Sehan University, Jeonnam, 526-702, Korea
[2]Department of Visual Optics, Baekseok University, Chonnan, 330-704, Korea

[†]Corresponding author : say@sehan.ac.kr
(Received : January 2, 2013, Revised : March 20, 2013, Accepted : March 25, 2013)

closely related with lenses' durability and is measured by the max. value of strength at which lenses are torn apart. In this study, functional contact lenses with high tensile strength by utilizing tris [2-(acryloyloxy)ethyl] isocyanurate and hexamethylene diisocyanate were produced and measured the durability of materials. Also, various physical properties of conventional contact lenses with various experiments including water contents were assessed.

## 2. Experimental Section

### 2.1. Polymerization

HEMA (2-hydroxyethyl methacrylate), NVP (n-vinyl-2-pyrrolidone) and MMA (methyl methacrylate) that are commonly used in soft contact lenses were used in copolymerization. Also, EGDMA(ethylene glycol dimethacrylate) was used to enhance bonding capability among monomers. To add functionality, tris [2-(acryloyloxy)ethyl] isocyanurateand hexamethylenediisocyanatewere mixed with different mixing ratios and stirred them in the motor speed 1700 r.p.m. for about 30 mins. Also, the polymerization temperature were 70°C for about 40 mins, 80°C for about 40 mins and 100°C for about 40 mins, respectively then processed them with thermal treatment to produce final products. Each sample was soaked in saline solution for about 24 hrs then their physical properties such as refractive index, light transmission, water content, and tensile strength were measured.

### 2.2. Equipment and Analysis

The refractive index was conducted based on ISO 18369-4:2006 (Ophthalmic optics - Contact lenses - Part 4: Physicochemical properties of contact lens materials, 4.5. Refractive index). For the accuracy of the test, the average value of three-times results for each sample was used. To measure light transmission, TOPCON TM-2 instrument was used. The water content was based on ISO 18369-4:2006 (Ophthalmic optics-Contact lenses-Part 4: Physicochemical properties of contact lens materials). The gravimetric method that put manufactured contact lenses in a glass bottle with $CaSO_4$, dried in the microwave oven for about 10 minutes, and hydrated them in saline solution of 0.90% sodium chloride for 24 hourswas used. The test method for tensile strengthwas to set the maximum value of the moment when lenses were torn apart as they received forces from 0.000 to 1.500 kgf for 0 to 20 seconds as the tensile strength values.

### 2.3. Reagents and Materials

Tris [2-(acryloyloxy)ethyl] isocyanurateto increase functionalities was used from Aldrich whileusing hexamethylenediisocyanate from Wako and the structure of each material was shown in Fig. 1. For an initiator that is used to polymerize with HEMA (2-hydroxyethyl methacrylate), commonly used as the major material of contact lenses, AIBN (azobisisobutyronitrile) of JUNSEIwas used.

## 3. Results and discussion

### 3.1. Mixing Ratio of Materials

The produced high performance copolymer made up of HEMA (2-hydroxyethyl methacrylate, 96.20%), NVP (n-vinyl-pyrrolidone, 2.50%), MMA (methyl methacrylate, 1.00%) and EGDMA (ethylene glycol

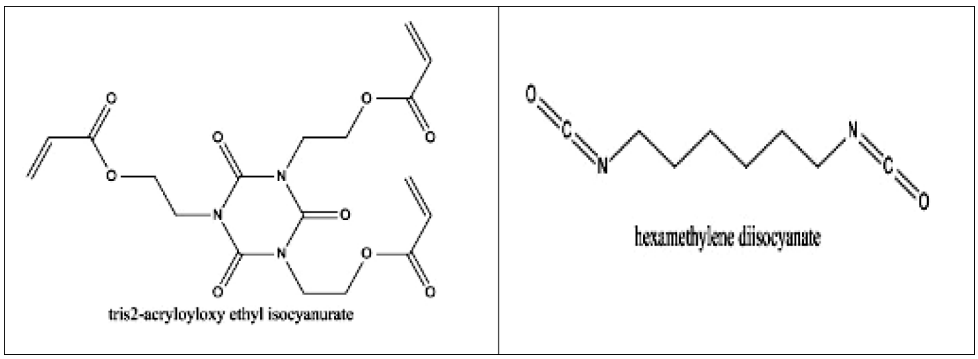



Fig. 1. Structures of additives

Table 1. Percent composition of samples with tris [2-(acryloyloxy) ethyl]isocyanurate

unit: %

| | HEMA | NVP | MMA | EGDMA | Tris [2-(acryloyloxy)] ethyl isocyanurate |
|---|---|---|---|---|---|
| Ref. | 96.20 | 2.50 | 1.00 | 0.30 | - |
| TRIS1 | 95.28 | 2.45 | 0.98 | 0.29 | 0.99 |
| TRIS3 | 93.45 | 2.37 | 0.96 | 0.29 | 2.92 |
| TRIS5 | 91.67 | 2.32 | 0.95 | 0.28 | 4.77 |
| TRIS7 | 89.96 | 2.28 | 0.94 | 0.27 | 6.55 |
| TRIS10 | 87.50 | 2.22 | 0.91 | 0.27 | 9.10 |

Table 2. Percent composition of samples with hexamethylenediisocyanate

unit: %

| | HEMA | NVP | MMA | EGDMA | Hexamethylenediisocyanate |
|---|---|---|---|---|---|
| HEXA1 | 95.28 | 2.45 | 0.98 | 0.29 | 0.99 |
| HEXA3 | 93.45 | 2.37 | 0.96 | 0.29 | 2.92 |
| HEXA5 | 91.67 | 2.32 | 0.95 | 0.28 | 4.77 |
| HEXA7 | 89.96 | 2.28 | 0.94 | 0.27 | 6.55 |
| HEXA10 | 87.50 | 2.22 | 0.91 | 0.27 | 9.10 |

dimethacrylate, 0.30%) without additional functional materials such as tris[2-(acryloyloxy)ethyl] isocyanurateand hexamethylenediisocyanatewas named as Ref. Also, with the basic mix of Ref., tris [2-(acryloyloxy)ethyl]isocyanuratewas added and gradually the quantities increased from 1.00 to 10.00% and named them as TRIS1 to TRIS10, which are summed up in the Table 1. Also, the samples produced by different proportion of hexamethylenediisocyanate ranging from 1.00 to 10.00% were named as HEXA1, HEXA3, HEXA5, HEXA7, and HEXA1 and were shown in the Table 2.

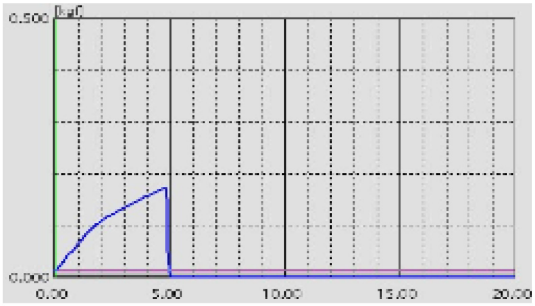
### 3.2. Tensile Strength

The tensile strength of the functional contact lenses produced by polymerization was obtained by measuring the moment of instant destruction of sample lenses as they received constant forces for about zero to 20 seconds after hydrating in 0.90% sodium chloride of saline solution for about 24 hours then removed their moisture. The average value of the sample was shown in Table 3 and Fig. 2. Tensile strength is one of the methods to measure the durability of lenses. Normally, the tensile strengths of soft contact lenses have about 0.100 to 0.200 kgf. It was found that the tensile strength of the contact lenses produced in this experiment is equivalent to those of conventional hydrogel contact lenses. Also, it was possible to confirm the flexibility of the produced lenses by calculating the slope of tensile strength represented in the graph. The tensile strength of the sample Ref. was 0.165 kgf, similar to that of common contact lenses, and had the lowest tensile strength in the produced samples. In the case of sample HEXA10, it has the highest tensile strength with 1.742 kgf. The average value of sample TRIS1 to TRIS10 that was made by adding different proportion of tris [2-(acryloyloxy)ethyl] isocyanuratefrom 1.00 to

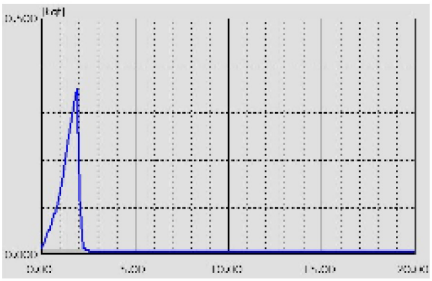
Table 3. Physical properties of samples (Tensile strength)

unit: kgf

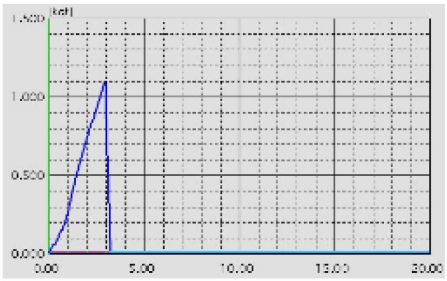
| Sample | Tensile strength |
|---|---|
| | Avg. |
| Ref. | 0.165 |
| TRIS1 | 0.285 |
| TRIS3 | 0.312 |
| TRIS5 | 0.327 |
| TRIS7 | 0.368 |
| TRIS10 | 0.612 |
| HEXA1 | 0.267 |
| HEXA3 | 0.485 |
| HEXA5 | 0.786 |
| HEXA7 | 1.255 |
| HEXA10 | 1.742 |




(a) Ref.



(b) TRIS7




(c) HEXA7

Fig. 2. Tensile strength of samples (Ref., TRIS7 and HEXA7)

10.00% was between 0.285 and 0.612 kgf and showed an upturn trend with the increasing quantity of MMA. Also, the average value of sample HEXA1 to HEXA10 that are made by adding different proportion of hexamethylenediisocyanate from 1.00 to 10.00% ranges from 0.267 to 1.742 kgf with gradually increasing trend with more hexamethylenediisocyanate.

It was also revealed that when tris [2-(acryloyloxy)ethyl] isocyanuratewas added, the tensile strength was somewhat increased with 10.00%. Also, comparing the same quantity of tris [2-(acryloyloxy)ethyl] isocyanuratewith hexamethylenediisocyanate, it showed that the increase in tensile strength is higher in hexamethylenediisocyanate than the other.

### 3.3. Refractive Index

Among physical property assessment, a refractive index is a constant that indicates the degree of refraction of light when it passes through a medium. Also, contact lenses made up of a material with high refractive index can reduce a gap between a power curve and a base curve, thereby allowing production of thinner lenses. The high polymers by soaking them in a saline solution for about 24 hours were hydrated to measure refractive index. The average value of the refractive index is shown in Table 4 and Fig. 3. The sample Ref. has the lowest refractive index with 1.434 whereas the sample HEXA10 with 10.00% hexamethylenediisocyanate showed the highest refractive index of 1.475. The average value of the sample TRIS that added 1.00 to 10.00% of tris [2-(acryloyloxy)ethyl] isocyanurateafter hydration ranged from 1.441 to 1.449. The average

Table 4. Physical properties of samples (Refractive index)

| Sample | Refractive index |
|---|---|
| | Avg. |
| Ref. | 1.434 |
| TRIS1 | 1.441 |
| TRIS3 | 1.443 |
| TRIS5 | 1.445 |
| TRIS7 | 1.447 |
| TRIS10 | 1.449 |
| HEXA1 | 1.443 |
| HEXA3 | 1.451 |
| HEXA5 | 1.458 |
| HEXA7 | 1.464 |
| HEXA10 | 1.475 |

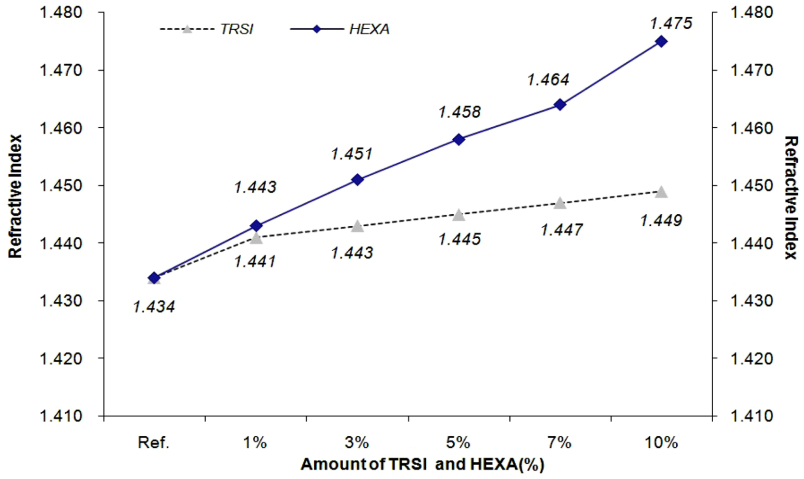



Fig. 3. Distribution of refractive index

refractive index value of sample HEXA that has increasing proportion of hexamethylenediisocyanate from 1.00 to 10.00% was between 1.443 and 1.475.

Comparing the same quantity of tris [2-(acryloyloxy)ethyl] isocyanuratewith hexamethylenediisocyanate sample, the growth of refractive index is larger in hexamethylenediisocyanate than the other.

### 3.4. Optical Transmittance

The optical transmittance is the degree in which light penetrates a certain medium expressed in percentage and is one of the most important physical properties for hydrogel contact lenses. In this study, the light transmittances for UV-B within the area of 290 nm to 320 nm and UV-A in the area of 320 nm to 400 nm and visible ray area between 380 nm and 720 nm were measured against the manufactured high performance polymers.

To measure light transmittance, samples were soaked in 0.90% of sodium chloride saline solution for about 24 hours, and the average value of light transmittance was shown in Table 5. The average light transmisstanceof UV-B, UV-A and visible rays on the sample was 80.3%, 87.5%, and 91.5% respectively.

Table 5. Optical transmittance of samples

unit: %

| Sample | | UV-B | UV-A | Visible rays |
|---|---|---|---|---|
| Ref. | Avg. | 80.3 | 87.5 | 91.5 |
| TRIS1 | Avg. | 80.1 | 84.6 | 90.2 |
| TRIS3 | Avg. | 79.8 | 84.5 | 89.8 |
| TRIS5 | Avg. | 79.4 | 83.6 | 88.8 |
| TRIS7 | Avg. | 78.6 | 81.6 | 87.5 |
| TRIS10 | Avg. | 75.9 | 80.5 | 85.6 |
| HEXA1 | Avg. | 78.2 | 85.5 | 90.2 |
| HEXA3 | Avg. | 75.5 | 84.1 | 89.8 |
| HEXA5 | Avg. | 73.5 | 81.5 | 86.5 |
| HEXA7 | Avg. | 70.6 | 78.5 | 85.6 |
| HEXA10 | Avg. | 70.3 | 77.8 | 84.9 |

### 3.5. Water Content

To measure the water content of the copolymer, the gravimetric method was used and the average value of the measured water content and the graph on the changes are shown in Fig. 4. The water content of the sample Ref. was 39.29%, equivalent to conventional contact lenses and the highest water content in the man-

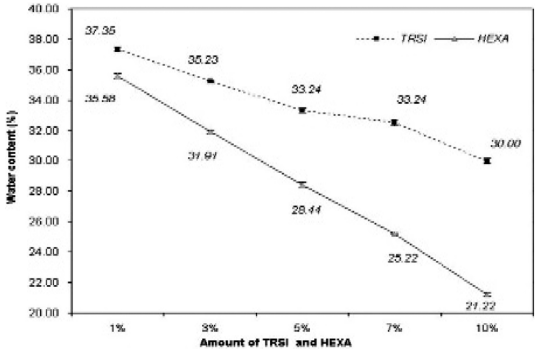



Fig. 4. Distribution of water content with soft lens samples

ufactured samples. The water content of the sample HEXA10 was 21.22%, the lowest in all samples. The water contents of the sample TRIS1 to TRIS10 that added different proportion of tris [2-(acryloyloxy)ethyl] isocyanuratefrom 1.00 to 10.00% were found to be in the range of 30.00 to 37.35%. Also, it was found that the water content of sample HEXA1 ~ HEXA10 that added different proportion of hexamethylenediisocyanate from 1.00 to 10.00% ranged from 21.22 to 35.58%. The distribution trend of water content showed that when the same amount of tris [2-(acryloyloxy)ethyl] isocyanurateand hexamethylenediisocyanate were applied the water content tended to fall with the increase in hexamethylenediisocyanate.

## 4. Conclusion

HEMA (2-hydroxyethyl methacrylate) common soft lens material, NVP (n-vinyl-2-pyrrolidone), MMA (methyl methacrylate) and EGDMA (ethylene glycol dimethacrylate) were used as basic mixture. Also, to increase tensile and mechanical strengths, it added polyurethane resins including isocyanate to copolymerize and measured the physical properties of the lenses so as to gauge their applicability as functional contact lenses. Also, tris [2-(acryloyloxy)ethyl] isocyanurate and hexamethylenediisocyanate were used and hydrogel lenses with copolymer was produced by means of the cast mould technique. Using the produced high performance polymers, the physical properties such as tensile strength, water content, light transmission and refractive index were measured and the applicability to soft hydrogel lenses were assessed. As a result, the average tensile strengths of samples TRIS1 to TRIS10 l that are obtained by varying quantities of tris [2-(acryloyloxy)ethyl] isocyanurate were between 0.285 and 0.612 kgf whereas those of the sample HEXA1~HEXA10 with varying quantities of hexamethylenediisocyanate were between 0.267 and 1.742 kgf, indicating that the higher the tensile strength, the larger the proportion of hexamethylenediisocyanate, compared with tris[2-(acryloyloxy)ethyl] isocyanurate. As for refractive index, the sample Ref. had the lowest refractive index of 1.434, while the sample HEXA10 that added 10.00% of hexamethylenediisocyanate has the highest refractive index of 1.475. The average value of refractive index of the sample TRIS that was supplemented with a different quantity of tris [2-(acryloyloxy)ethyl] isocyanurate from1.00 to 10.00% had a range between 1.441 and 1.449, whereas the average refractive index value of the sample HEXA made by gradually increasing proportion of hexamethylenediisocyanate from 1.00 to 10.00% were between 1.443 to 1.475. When comparing between the identical quantity of tris [2-(acryloyloxy)ethyl] isocyanurate and hexamethylenediisocyanate samples, it revealed that the higher the quantity of hexamethylenediisocyanate, the higher the increase in refractive index. The light transmittances of the sample TRIS1 to TRIS10 were: 75.9 ~ 80.3% for UV-B, 80.5 ~ 87.5% for UV-A and 85.6 ~ 91.5% for visible rays. In case of those of the sample HEXA1 to HEXA10 were: 70.3 ~ 78.2% for UV-B, 77.8 ~ 85.5% for UV-A and 84.9 ~ 90.2% for visible rays, indicating satisfactory visible ray transmission of conventional hydrogel contact lenses. The water contents measured by the gravimetric method were as follows: for the sample TRIS1 to TRIS10, the water content ranged from 30.00 to 37.35%; for the sample HEXA1 ~ HEXA10, it was between 21.22 and 35.58%. Theseresults showed the possibility of functional contact lenses with excellent tensile strength and mechanical properties by adding isocyanate to the hydrogel contact lens materials.

## Acknowledgements

This research was financially supported by Ministry of Knowledge Economy(MKE) and Korea Evaluation Institute of Industrial Technology(KEIT) through the Project of Standard Technology Development

## References

[1] K. W. Gellatly, N. A. Brennan, and N. Efron, “Visual decrement with deposit accumulation of HEMA contact lenses”, Am. J. Optom. Phys. Opt., Vol. 65, pp. 937-941, 1988.

[2] C. E. Soltys-Robitaille, D. M. AmmonJr.,and P. L. GrobeJr., “The relationship between contact lens surface charge and in-vitro protein deposition levels”, Biomaterials, Vol. 22, pp. 3257-3260, 2001.

[3] M. G. Baines, F. Cai, and H. A. Backman,“Adsorption and removal of protein bound to hydrogel contact lenses”, Optom. Vis. Sci., Vol. 67, pp. 807-810, 1990.

[4] V. Compan, A. Andrio, A. López-Alemany, E.

Riande, and M. F. Refojo, "Oxygen permeability of hydrogel contact lenses with organosilicon moieties", Biomaterials, Vol. 23, pp. 2767-2772, 2002.

[5] B. A. Holden and G. W. Mertz, "Critical oxygen levels to avoid corneal edema for daily and extended wear contact lenses", Invest.Ophth. Vis. Sci., Vol. 25, pp. 1161-1167, 1984.

[6] E. B. Papas, C. M. Vajdic, R. Austen, and B. A. Holden, "High-oxygen-transmissibility soft contact lenses do not induce limbalhyperaemia", Curr. Eye Res.,Vol. 16, pp. 942-948, 1997.

[7] R. M. Hill and I. Fatt, "Oxygen uptake from a reservoir of limited volume by the human cornea in vivo", Science, Vol. 142, pp. 1295-1297, 1963.

[8] T. H. Kim and A. Y. Sung, "Copolymerization and contact lens application of HEMA-substituted polyphosphazene", J. Kor. Chem. Soc., Vol. 53, pp. 340-344, 2009.

[9] K. H. Ye, S. H. Cho, and A. Y. Sung, "Study on the antibiosis and physical properties of copolymer containing silver", J. Kor. Chem. Soc., Vol. 53, pp. 542-546, 2009.

[10] T. H. Kim, K. H. Ye, and A. Y. Sung, "A study on the measurement of water content in hydrogel contact lens by gravimetric method", J. Korean Oph. Opt. Soc., Vol. 13, pp. 59-63, 2008.

[11] T. H. Kim, K. H. Ye, Y. S. Kwon, and A. Y. Sung, "Polymerization of contact lens materials using silicone", J. Korean Oph. Opt. Soc., Vol. 11, pp. 143-159, 2006.