Journal of Photoscience (2002), Vol. 9(1), pp. 23–28

Polymaleimide Copolymers with Norbornane units for Polymeric Optical Waveguides†

Won Lae Kim, Chul Joo Lee, Kwan Soo Han[1], Hak Soo Han[2] and Ki Hong Park*
Electronic Materials and Devices Research Center, KIST, Seoul 136-791, Korea
[1]R&D center, Luvantix, Seoul 135-090, Korea
[2]Division of Chemical Engineering, Yonsei University, Seoul 120-749, Korea

In order to obtain thermal-stable, low birefringent, and low optical loss waveguiding materials, we synthesized several fluorinated poly(maleimide-*co*-glycidylmethacrylate)s using a pentafluorophenylmaleimide (PFM) and two kinds of methacrylate derivatives as comonomers and glycidylmethacrylate as a crosslinker. One comonomer is a linear fluorinated methacrylate (HFBM) and another is a bulky norbornane-derived methacrylate (NMMA). These copolymers could be self-crosslinked by heating due to epoxy groups of glycidylmethacrylates. As a maleimide contents increased to 50 mol%, these copolymers showed high decomposition temperatures of above 300°C. The refractive index could be precisely controlled by the variation of PFM/HFBA or PFM/NMMA feed ratio in the range of 1.410~1.508 at 643 nm. The copolymers had very low birefringence in the range of $1\sim5\times10^{-4}$.

key words: low birefringence, norbornane, fluorinated polymers, optical waveguiding, polymaleimide

INTRODUCTION

There have been extensive researches for a variety of applications and materials in the area of optical communication systems. Inorganic materials have been mainly used in optical components such as optical waveguides in current communication systems. In the near future, polymeric optical materials are expected to be replaced for inorganic crystals and silica because of their potential advantages such as lower temperature processability and lower cost [1]. Polymeric materials are fairly soluble in organic solvents so optical films can be made easily by spin-casting of the polymer solution. In addition, they can be easily made to complicated waveguiding patterns by means of photolithography followed by reactive ion etching or by electron-beam lithography, and molding technology [2,3]. Polymeric optical waveguiding materials require high optical transparency in visible or near-infrared regions, good thermal stability, refractive index controllability, and low birefringence. It is well known that the intrinsic optical losses of polymers are attributed to absorption from the overtone of vibration stretching bands (2900 cm^{-1}) of C-H bonds. Therefore, the most conventional strategy to reduce intrinsic optical loss is the replacement of C-F bonds instead of C-H bonds [4]. A variety of optical waveguiding polymers with low loss have been developed using fluorinated polymers. Furthermore, thermally stable optical polymers are important in providing compatibility with conventional intercircuits fabrication process and in ensuring device reliability during high temperature operation [5]. Because the use of poly (methylmethacrylate) (PMMA)-based polymers is limited to below 80°C, polyaryleneethers and polyimides are very adaptable for high temperature applications [6]. Controllability of the refractive index is fundamental for optical components such as single-mode optical waveguides, which can be controlled by copolymerization with refractive index controllable monomers containing aromatic or fluoride units. Moreover, the difference between TE- and TM-mode refractive index should be minimize to prevent the distortion of output signals. Concerning about birefringences, aliphatic polymer such as PMMA seems more advantageous than aromatic polymers such as polyimides. However, aromatic polyaryleneethers and polyimides have relatively larger birefringences. On the other hand, aromatic polymers exhibited better thermal stability while PMMA exhibited worse thermal stability. Therefore, we must figure out the most appropriate optical polymeric materials with good balance of all required properties.

We have proposed that poly(maleimide) and poly(glycidylmethacrylate) could be a good candidate material for optical application [7,8]. Polymaleimides are expected to have better thermal stability than PMMA as well as lower birefringence than polyimides. Polyglycidylmethacrylate was known to be crosslinkable on heating. Crosslinkability after solvent casting is a very good merit for manufacture of multi-layers. In this study, in order to develop optical waveguiding materials with good thermal stability, low loss, and low birefringence, we synthesized several polymaleimide copolymers using fluorinated

† This paper is dedicated to Professor Sang Chul Shim of KAIST who has just passed away untimely.

*To whom correspondence should be addressed.
E-mail : khopark@kist.re.kr

Received January 12, 2002; accepted March 20, 2002

and norbornane derivatives. This bulky aliphatic norbornane unit is expected to be a good substituent for optical materials with low birefringence. We herein tried to search an appropriate copolymeric system with good balance of requirements for optical waveguiding materials. The copolymerization behavior, thermal properties, the controllability of refractive index, and their birefrigent properties were investigated.

EXPERIMENTAL

Materials. Maleic anhydride (MA), 2,3,4,5,6-pentafluoro aniline (PFA), 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBM), glycidyl methacrylate (GMA), 2-norbornanemethanol (NMOH), 1,1,2,2-tetrachloroethane (TCE), phosphorus pentoxide, triethylamine (TEA) was purchased from Aldrich Co. MA was purified by recrystallization, and HFBM was purified by distillation under vacuum. The PFA, NMOH, phosphorus pentoxide, and TEA were used without further purification. Methacryloyl chloride (MC) was purchased from Acros and used without purification. 2,2'-Azobis(2,4-dimethylvaleronitrile) (ADMVN) from Wako was recrystallized before use.

Synthesis of 1-(2,3,4,5,6-pentafluorophenyl)-2,5-dihydro-1H-2,5-pyrroledione (PFM). Into 250 mL two necked flask, added maleic anhydride (MA) 25 g (0.25 mol), 2,3,4,5,6-pentafluoroaniline (PFA) 25 g (0.14 mol), and 50 mL of *N,N*-dimethylformamide (DMF). In another 100 mL beaker, 7.45 g (52.49 mmol) of phosphorus pentoxide and 3.23 g (32.93 mmol) of sulfuric acid were dissolved in 10 mL of DMF with stirring. This phosphorus pentoxide solution was slowly added into the prepared MA/PFA solution and stirred at room temperature for 2 h and then at 110°C for 1 h. The reactant was poured into water to precipitate the product. The solid product was separated by filtration, and dried at vacuum oven for 24 h, and then purified from recrystallization (ethanol), giving white PFM crystals. Yield : 65%, m.p. : 107°C (by DSC) (ref. m.p. 105.5°C); IR: 1734 (C=O), 1530 (C=C aromatic), 1362 (C-N) cm^{-1} ; ^{1}H-NMR(DMSO-d_6): δ d 7.4 (CH=CH) ppm.

Synthesis of bicyclo[2.2.1]hept-2-ylmethyl 2-methylacrylate (NMMA). Into 500 mL flask, added 10 g (79.24 mmol) of 2-norbornanemethanol(NMOH) and 200 mL of chloroform. The portion of 9.94 g (95.09 mmol) of methacryloyl chloride (MC) was added into the solution and then triethylamine 20 mL was slowly added at room temperature. The solution was reacted at room temperature for 2 h, and at 40°C for 4 h. The reactant was extracted from chloroform/water, and the organic layer was dried with magnesium sulfate. The solvent was removed by evaporation, and the crude liquid was purified by silica gel column chromatography, yielding colorless liquid. Yield : 61%; IR: 1720 (C=O), 1638(C=C), and 1164 (C=O) cm^{-1}; ^{1}H-NMR(DMSO-d_6): δ 0.5~2.2 (m, norbornane), 1.9 (s, CH_3), and 5.7 and 6.0 ppm (d, CH_2=C) ppm).

Polymerization of poly(maleimide-co-glycidylmethacrylate). Three monomers (5 mmol each) were added in 30 mL polymerization ampoule and dissolved in 10 mL of 1,1,2,2-tetrachloroethane(TCE). The portion of 0.1 mol% of 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) against total monomer concentrations was added into polymerization solution. The oxygen in ampoule was removed by freeze-vacuum-thaw method. The solution was stirred at 40°C for 24 h, and poured into methanol to precipitate polymer, and washed thoroughly with methanol. The polymers were separated by filtration and dried in vacuum oven.

Characterization. FT-IR and ^{1}H-NMR (200 MHz) spectra were recorded on a Mattson Alpha Centauri spectrophotometer and a Varian Gemini 200 NMR spectrometer, respectively. Differential scanning calorimetry (DSC) was performed with a Dupont thermal analyzer DSC 2910 at a heating rate of 20 °C/min in nitrogen. Thermogravimetry (TG) was performed with a Dupont thermal analyzer DSC 2950 at a heating rate of 10°C/min in nitrogen. Gel Permeation Chromatography was performed by Waters HPLC system (model 510 pump, model 410 differential refractometer, PL Gel columns (HR2, HR4, HR5E)) using tetrahydrofuran and polystyrene standards. For the measurement of refractive index and birefriengence, about 25 wt% polymer solution was prepared in chlorobenzene, and filtrated by 0.45 μm PTFE syringe filter and spin casted onto slide glass. The polymer films were heated at 100°C for 24 h under vacuum. The refractive index (TE (transverse electric) and TM(transverse magnetic)) was determined by Prism Coupler (Model 2010, Metricon) at a wavelength of 642.8 nm (He-Ne laser), respectively.

RESULTS AND DISCUSSION

As shown in Figure 1, a fluorinated PFM monomer was synthesized by a reaction of maleic anhydride and 2,3,4,5,6-pentafluoro aniline (PFA) in presence of phosphorous pentoxide as a dehydrating agent. The NMMA comonomer was synthesized by a condensation reaction of methacryloyl chloride (MC) with 2-norbornanemethanol (NMOH). The synthesis of PFM

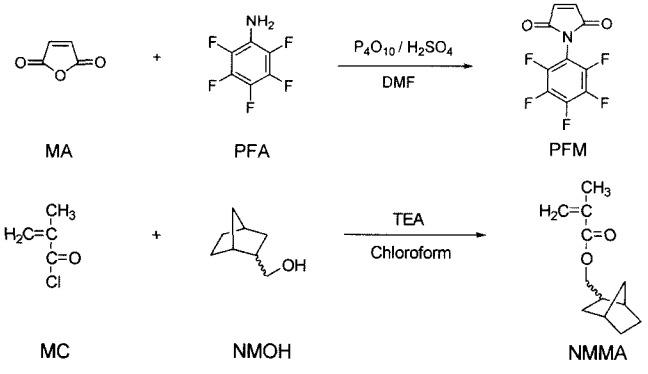

Figure 1. Synthesis of pentafluorophenyl methacrylate and norbornanemethyl methacrylate.

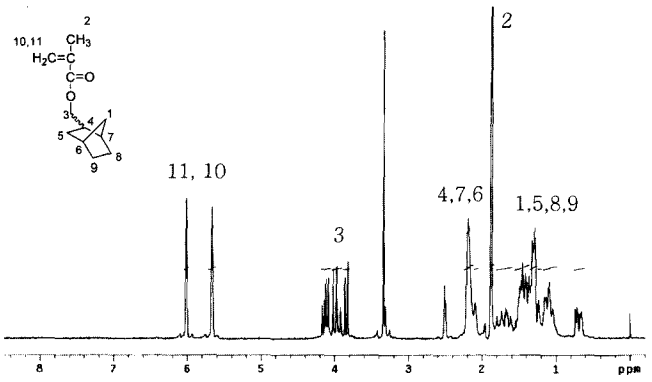

Figure 2. ^{1}H-NMR spectrum of NMMA monomer.

and NMMA monomers were characterized by FT-IR and ^{1}H-NMR spectroscopy. At ^{1}H-NMR spectrum of PFM, we could observe only two peaks at 7.4 ppm implying CH=CH of maleimide with fluorinated *N*-phenyl group. As shown in a ^{1}H -NMR spectrum of NMMA (Figure 2), there were multiple aliphatic peaks from norbornane moiety (0.5~2.2 ppm) and a sharp peak from methyl moiety (1.9 ppm), as well as two sharp peaks from vinyl moiety (5.7 and 6.0 ppm). The complicated aliphatic peaks are responsible for the *endo*- and *exo*- isomers of norbornanemethyl unit. We could confirm some infra-red characteristic absorption peaks of NMMA at 1720(C=O), 1638 (C=C), and 1164 (C-O) cm^{-1}. The PFM monomer was obtained as solid crystals while the NMMA as viscous liquid. The PFM monomer was expected to be an optical loss reducer without fatal decrease of refractive index due to phenyl group. The commercially available fluorinated monomer HFBM was used as an optical loss reducer. On the other hand, NMMA with bulky norbornane was designed for a refractive index increaser together with a birefringence reducer.

The polymer structures are shown in Figure 3. The copolymers were synthesized by general radical polymerizations at relatively low temperature of 40°C. The polymerizations were conducted in variety of two monomers composition while maintaining 10 mol% content of glycidyl methacrylate, as shown in Table 1. We used a specific radical initiator of 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN). The low temperature initiator, ADMVM was adopted for obtaining high molecular weight polymers and for prohibiting possible crosslinking reaction at polymerization temperature between epoxy rings in this polymerization system. All the polymerizations were carried out effectively even at 40°C, we could obtain white polymer solids with moderate molecular weight in all polymerization. As summarized in Table 2, the number-average molecular weights by GPC measurement were in the range of 190,000 ~360,000 except in the highest PFM content (90%). The low molecular weight of the 90% PFM system was responsible for the lower reactivity of PFM monomer than that of methacrylate monomers. Comparing molecular weights of HFBM series with those of NMMA, the molecular weight of NMMA-derived

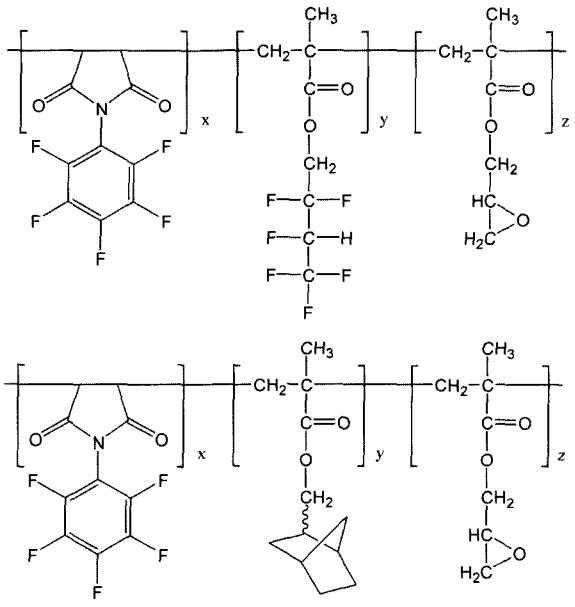

Figure 3. Structures of copolymers in this study.

Table 1. Physical properties of polymers

	Feed ratio(mol %)			T_d,[a] 5 wt% (°C)	M_n[b]	M_w/M_n[b]
	PFM	HFBM or NMMA	GMA			
PPFM	90	0	10	317	58,000	5.90
HFBM Series	60	30	10	343	240,000	2.02
	40	50	10	336	190,000	2.70
	20	70	10	307	210,000	2.01
	0	90	10	258	200,000	1.85
NMMA Series	60	30	10	359	290,000	2.77
	40	50	10	353	270,000	2.77
	20	70	10	335	370,000	2.60
	0	90	10	231	360,000	2.96

a) measured by TG at a heating rate of 10°C/min.
b) measured by GPC using polystyrene standards.

Table 2. The birefringence of polymers

PFM contents (%)	Birefringence[a]	
	HFBM series	NMMA series
90	0.0005	0.0005
60	0.0005	0.0002
40	0.0002	0.0002
20	0.0001	0.0001
0	0.0001	< 0.0001

a) measured by prism coupler

polymer were a little higher. These moderate molecular weights of the copolymers are expected to be very advantageous for reliable film manufacture of waveguiding materials. The HFBM copolymer series were expected to be low optical loss materials

because of their high content of fluoride. In this study, however, we did not measure the optical losses of the copolymers because we focused on the enhancement of thermal stability and the controllability of refractive indexes of polymers.

We attempted to measure the glass transition temperatures by means of DSC, however, which of all the copolymers could not be detected on DSC curves. We could observe a broad exothermic peak in the range of 150~250°C as shown in Figure 4 and Figure 5. It may be because these copolymers reacted between epoxy rings on heating, yielding crosslinked polymers. The another evidence of intermolecular crosslinking between polymer chains on heating was the solubility change. The polymer cast films were fairly soluble in organic solvents like tetrahydrofuran and chloroform, but those after heating showed poor solubility in solvents. This solubility change on heating can be very advantageous for multi-layer coating because the top surface of the bottom layer after heat treatment would not be destroyed by a solvent of top layer solution. The thermogravimetric (TG) curves of PFM/HFBM/GMA and PFM/NMMA/GMA series are displayed in Figure 6 and Figure 7, respectively. The 5 wt% weight loss temperatures of the copolymers were measured by thermogravimetric analysis (TGA) and summarized in Table 1. As PFM content increased, the thermal stability increased remarkably. The copolymer without PFM began to decompose around 200~250°C, however, the initial decomposition temperature of a PFM/NMMA(or HFBM)/GMA (60/30/10) copolymer, was above 300°C.

All these copolymers exhibited high solubility in organic

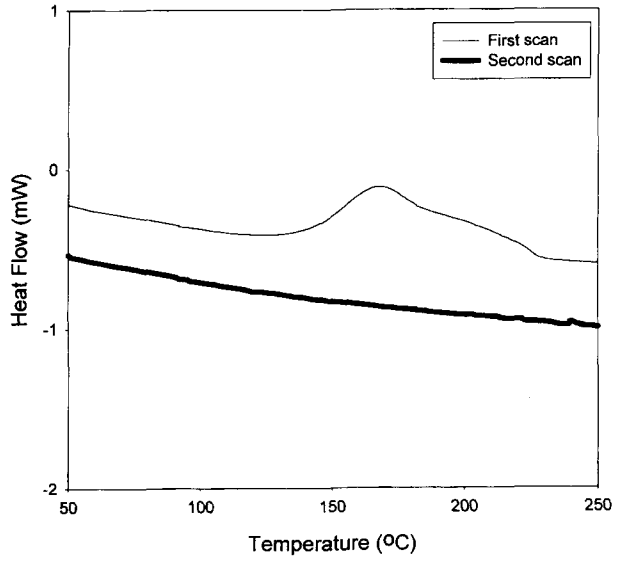

Figure 4. DSC curves of the polymer with 50% HFBM.

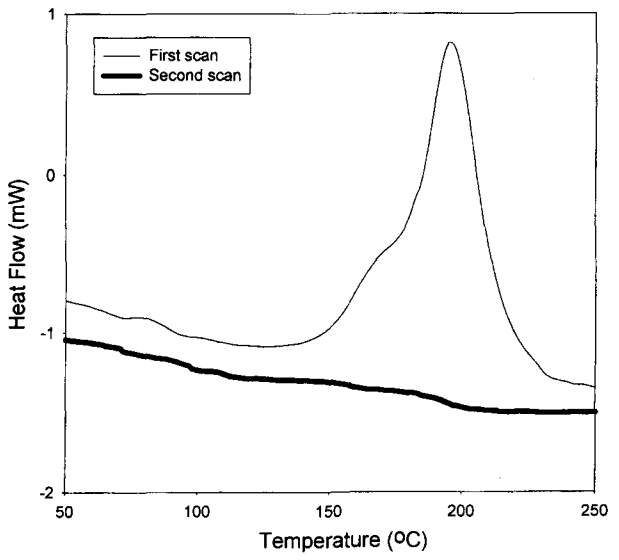

Figure 5. DSC curves of the polymer with 50% NMMA.

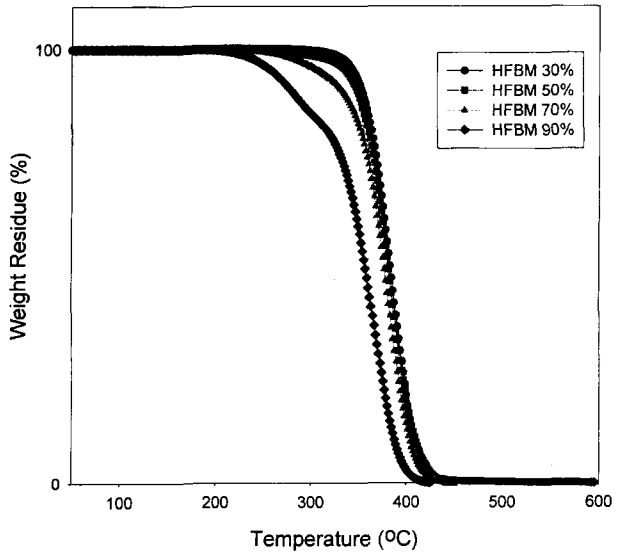

Figure 6. TGA curves of HFBM-derived copolymer series.

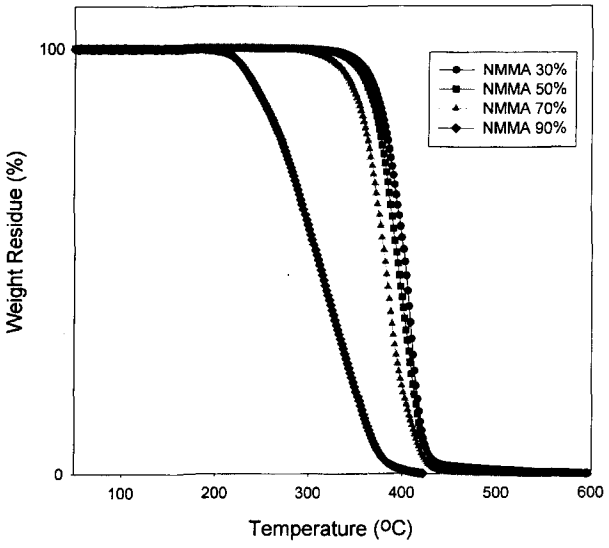

Figure 7. TGA curves of NMMA-derived copolymer series.

solvents such as tetrahydrofuran, chlorobenzene, and chloroform, etc. The casting solution was prepared using 10 wt% chlorobenzene solution. The optically transparent polymer films with thickness of 2~5 μm were successfully prepared onto slide glass by spin casting.

The refractive indexes of these polymer films were measured by Metricon at a wavelength of 642.8 nm. Figure 8 and Figure 9 show the dependence of refractive index on PFM content in HFBA and NMMA polymer series, respectively. In both cases, it was found that the refractive index was linearly increased or decreased in terms of PFM content. This means that this copolymer system can be precisely controlled by changing monomer feed ratio so that we can obtain optical waveguiding materials with desirable refractive index. Generally, it is well known that the refractive index decreases as fluoride content increases. In PFM/HFMA polymer series, two monomers (PFM and HFBA) contain fluoride moiety. The refractive index as shown in Figure 8, increased in the range of 1.410~1.430 as PFM content increased. This phenomenon was attributed to higher refractive index of bulky PFM unit than that of linear HFBA unit. In contrast, the refractive index of NMMA polymer series decreased in the narrower range of 1.509~1.501 as PFM content increased because NMMA units did not have fluoride. The change of refractive indexes at NMMA series was smaller than those of HFBM series. This result means that the refractive index change of PFM/HFBM/GMA series are less dependant on feed ratio, so that copolymers with more reproducible refractive indexes can be synthesized regardless of three monomer composition in this system.

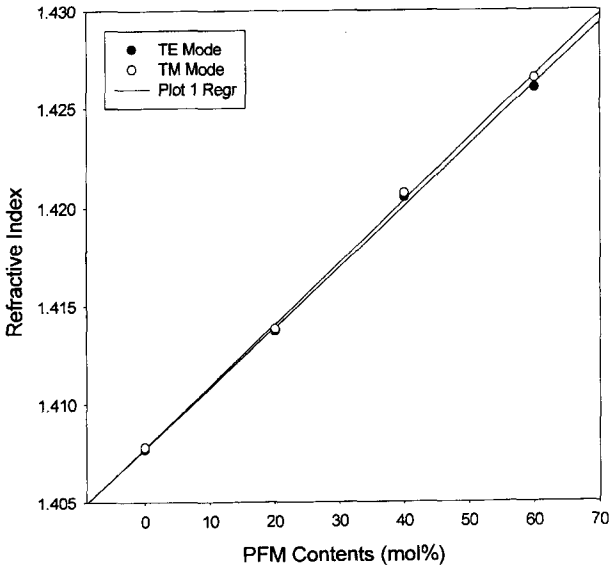

Figure 8. TE and TM-mode refractive indices of HFBM series depending on PFM content.

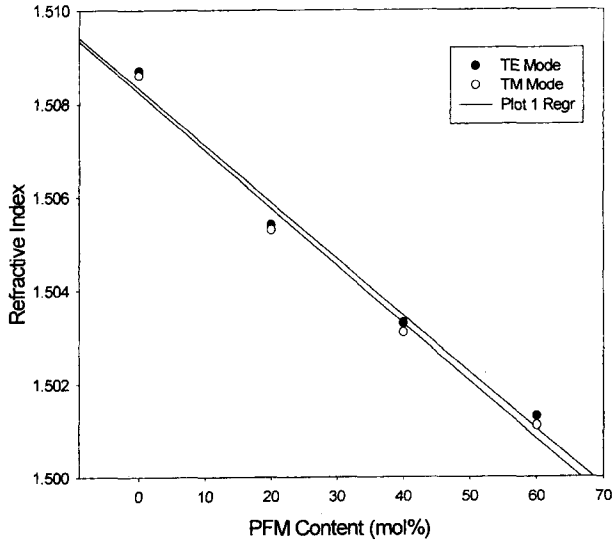

Figure 9. TE and TM-mode refractive indices of NMMA series depending on PFM content.

The birefringences were estimated by the difference between TE-mode and TM-mode refractive indexes and summarized in Table 2. As a result, the birefringence increased gradually from 0.0001 to 0.0005 in terms of PFM content. The reason why the birefringence of PFM/HFBA/GMA (90/0/10) polymer was almost the same as that of PFM/HFBA/GMA (60/30/10) polymer, might be due to lower reactivity of PFM than GMA, so PFM/HFBA/GMA (90/0/10) polymer did not contain as much as the feeding amount of PFM. It was very noteworthy that both of HFBA and NMMA series exhibited very low birefringence even though these polymers contained rigid maleimide backbone and planar phenyl unit. Conclusively, the HFBA and NMMA comonomers acted on great role for reducing birefringence of polymaleimide copolymers.

CONCLUSIONS

In order to prepare optical waveguiding polymers with a good property balance, we synthesized several fluorinated maleimide-glycidylmethacrylate copolymers by radical polymerization using a low temperature initiator of 2,2'-azobis(2,4-dimethylvaleronitrile). A monomer, *N*-pentafluorophenylmaleimide and two kinds of comonomers with fluorinated alkyl and bulky norbornane unit were used for thermally stability, low optical loss and low birefringence. The introduction of maleimide unit enhanced thermal decomposition temperatures. These copolymers after heat treatment were insoluble in organic solvents, implying intermolecular crosslinking between epoxy rings. The refractive index of copolymers could be precisely controlled by the composition of maleimide/comonomers. The copolymers had very low birefringences in the range of $1\sim5\times10^{-4}$. Some polymaleimide copolymers in this study can be good candidates because these copolymers satisfied with most of requirements of optical waveguiding materials such as thermal stability, cross-linkability, refractive index controllability, and low birefringence.

Acknowledgements – This research was supported by a KOSEF grant (R01-200-00338).

REFERENCES

1. L. Eldada, R. Blomquist, L. W. Shacklette and M. McFarland (2000) High-Performance Polymeric Componentry for Telecom and Datacom Applications. *Opt. Eng.*, **39**, 596-609.
2. T. Matsuura, S. Ando and Sasaki, F. Yamamoto (1993) Heat-Resistent Singlemode Optical Waveguides Using Fluorinated Polyimides. *Electron. Lett.*, **29**, 269-270.
3. Y. Y. Maruo, S. Sasaki and T. Tamamura (1995) Channel-Optical-Waveguide Fabrication Based on Electron-Beam Irradiation of Polyimides. *Appl. Opt.*, **34**, 1047-1052.
4. C. Pitois, S. Vukmirovic, A. Hult, D. Wiesmann and M. Robertsson (1999) Low-Loss Passive Optical Waveguides Based on Photosensitive Poly(pentafluorostryrene-co-glycidyl methacrylate). *Macromolecules*, **32**, 2904-2909.
5. M. Usui, M. Hikita, T. Watanabe, M. Amano, S. Sugawara, S. Hayashida and S. Imamura (1996) Low-Loss Passive Polymer Optical Waveguides with High Environmental Stability. *J. Lightwave Technol.*, **14**, 2338-2343.
6. R. Reuter, H. Franke and C. Feger (1988) Evaluating Polyimides as Lightguide Materials. *Appl. Opt.*, **27**, 4565-4571.
7. K. H. Park, J. T. Lim, S. Song, M. K. Kwak, C. J. Lee and N. Kim (1999) Nonlinear Optical Polymers with Novel Benzoxazole Chromophores IV. Synthesis of Maleimide-Styrene and Maleimide-Methacrylate Copolymers. *React. and Funct. Polym.*, **40**, 169-175.
8. K. H. Park, M. K. Kwak, Y. S. Lee, W. S. Jahng, C. J. Lee and N. Kim (1999) Nonlinear Optical Polymers with Novel Benzoxazole Chromophores III. Synthesis and Characterization of Self-Crosslinkable Glycidylmethacrylate Copolymers. *React. and Funct. Polym.*, **40**, 41-49.