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Physical Properties of Polymethylsilsesquioxane with UV-Curable Group for Low-Loss Optical Materials

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*Polymethylsilsesquioxane(PMSQ)s with photo-curable groups were prepared by copolymerization of alkoxysilanes. Poly(acryloyl-*co*-methylsilsesquioxane) (PAMSQ)s of various mole ratio acryloyl group (6 mol%, 12 mol%, 24 mol%, 48 mol%, 100 mol%) were obtained from copolymerization of methyltrimethoxylsilane and 3-(trimethoxysilyl)propyl acrylate. Optical and photonic curable properties were studied by near infrared region spectra, prism coupler, UV-visible spectra, and photo-DSC. The optical losses were below 0.002 dB/cm at 830, 1330, and 1550 nm, respectively. Optical loss was found to be independent of a molar ratio of functional group.*

Keywords Cross-link; optical loss; polymethylsilsesquioxane; thermal stability; UV-curable group; waveguide

Introduction

Over the last two decades, advances in electronic devices have revolutionized the speed that we perform computing and communication of all kinds. Three key technologies were combined to create a platform that enabled the electronic revolution: semiconductor materials, automated microfabrication of integrated electronic circuits, and integrated circuit design. As a result, the mass manufacturing of low-cost integrated circuits has become possible. However, bandwidth demand is outgrowing the performance of electronics for many applications. Signal propagation and switching speeds in the electronic domain are inherently limited. One area where these limitations are clearly seen is in telecommunications, where bandwidth expansion is desperately needed. To overcome these barriers, we must enter a new

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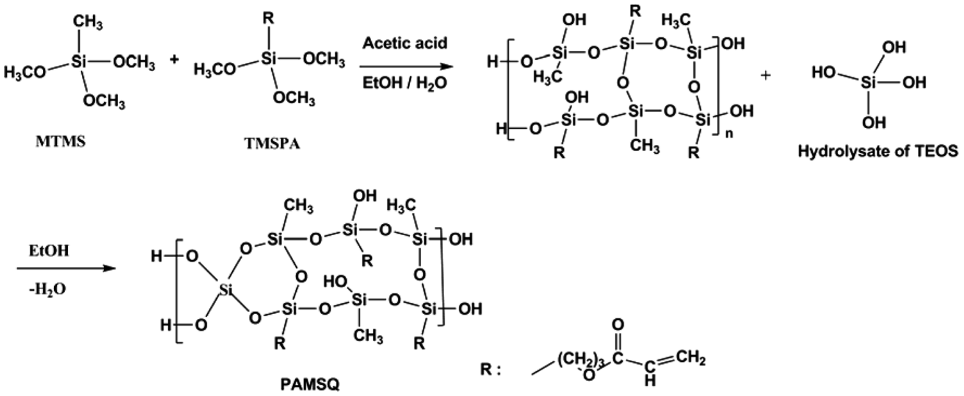

Scheme 1. Synthesis of polymethylsilsesquioxane with UV-curable group.

computing and communications revolution based on photonics application having an extremely large information capacity and very low transmission loss and heat generation [1].

To keep pace with these requirements, the preparation of light-guiding polymers applicable in photonics began in the 1970s [2]. Examples of such optical polymers include deuterated and halogenated polyacrylates [3], fluorinated polyimides [4], perfluorocyclobutyl (PFCB) aryl ether polymers [5], and nonlinearoptical polymers [6]. And even though these optical polymers are successfully synthesized with high transparent and low optical loss at 840, 1310, and 1550 nm, they have problems arising from intrinsic properties of florin and low heat durability. It might become a cause of the bad fabrication of light-guiding film. To compensate for these problems, inorganic-organic hybrid polymers have been developed and tested for evaluation. Especially, this hybridization of inorganic-organic polymer is spotlighted to fabricate waveguide in low optical loss and thermal stability.

This paper focused on physical properties of polymethylsilsesquioxanes with UV-curable functional groups. Double chained siloxanes with high heat resistance were compared to common optical polymers, and methyl groups gave low optical losses. It is also maximizing the fabrication speed as UV-curable group was taken part in molecule kind of acryloyl groups. Poly(acryloly-*co*-methyl silsesquioxane) (PAMSQ)s were prepared with various mol ratio (6 mol%, 12 mol%, 24 mol%, 48 mol%, 100 mol%) of acryloyl group from methyltrimethoxylsilane and 3-(trimethoxysilyl)propyl acrylate (Scheme 1). Optical and photo-curable properties were shown by near infrared region spectra, prism coupler, UV-visible spectra and photo-DSC.

Experimental

Materials

All the reagents and solvents were commercially available and of analytical grade. Methyltrimethoxysilane (MTMS) and tetraethyl othosilicate (TEOS) were purchased from Aldrich Company. 3-(Trimethoxysilyl)propyl acrylate (TMSPA) and hydrochloric acid (HCl) were purchased from TCI company. Ethyl alcohols, acetic acid

Table 1. Various mol ratios of PAMSQs

	MTMS	TMSPA
PAMSQ-I (6 mol%)	50.36 ml (0.353 mol)	5.46 ml (0.023 mol)
PAMSQ-II (12 mol%)	47.07 ml (0.33 mol)	10.68 ml (0.045 mol)
PAMSQ-III (24 mol%)	40.65 ml (0.285 mol)	15.16 ml (0.09 mol)
PAMSQ-IV (48 mol%)	27.81 ml (0.195 mol)	42.72 ml (0.18 mol)

and magnesium sulfate anhydrous were from Daejung company. Distilled water was used in hydrolysis.

Characterization

The properties of materials were demonstrated by thermogravimetric analysis (TGA), the photonic differential scanning calorimeter (Photo-DSC), UV-visible spectrometer, near IR spectrometer and prism coupler. TGA was carried out by Du Pont TGA 2950. The temperature ranged from 50 to 800°C and the heating rate was 10°C/min. Photo-DSC was performed utilizing the Q100 DSC modified with the photocalorimeter accessory (PCA) and its intensity was approximately 10 mW/cm^2 in atmosphere. The UV/Vis/NIR spectra were recorded by Jasco V-570. A Metricon Model 2100 prism coupler was used to measure the thin film at wavelength of 632.8 nm.

Preparing of Hydrolysate of Tetraethyl Othosilicate (TEOS)

72 mL (4 mol) of water and 2 g of hydrochloric acid (35 wt% in H_2O) were stirred in 28 mL ethanol for 30 min. 41.6 g (0.2 mol) of TEOS was slowly dropped into the mixture solution with vigorous stirring. After adding the TEOS, it was allowed to reacting for 24 h at room temperature and then directly proceeded to next step without any treatment.

*Preparing of Poly(acryloyl-*co*-methyl silsesquioxane)(PAMSQ) of Various Molar Ratio of Acryloyl Group*

65.21 mL (3.62 mol) of water and 4.62 g acetic acid were stirred in 75.35 mL of ethanol for 30 min. Mixed monomer of MTMS and TMSPA as shown in Table 1 was slowly added in the solution. The reactants were stirred at room temperature for 24 hours. After 2.87 g of hydrolysate of TEOS was added into the solution, they were reacted further at room temperature for 24 hours. The product was extracted by ether and water to remove acid. After that, water was eliminated by magnesium sulfate anhydrous. The dried ether solution was evaporated by aspirator. The final product was obtained as a viscous light yellow liquid.

Results and Discussion

Characterization of UV-Curable Properties of PAMSQs

The optimum condition of photo polymerization is decided by the heat differentiation of photo-DSC curves. In the curves of photo-DSC, peak maximum values

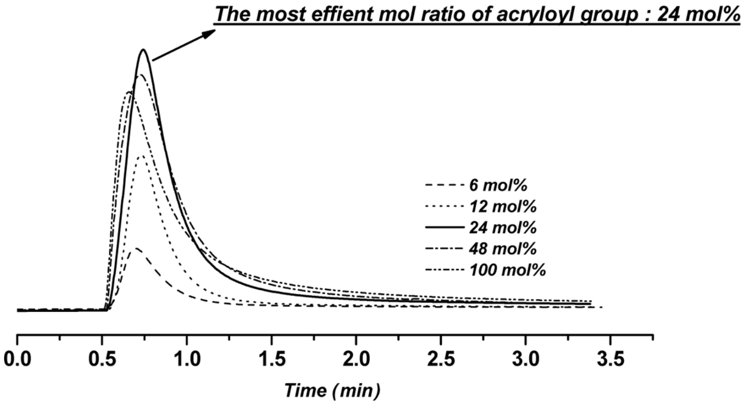

Figure 1. Photo-DSC curves of PAMSQs with various acryl mol ratio.

have shown to be the most efficient condition of photopolymerization [7]. Using this analysis method, various mol ratios of PAMSQs were carried out to measure the photo-DSC whether more acryloly groups had higher heat differentiation or not. Irgacure-184, a hydroxyalkylphenon compound, was used as photo-initiator. The amount of photo-initiator was arbitrarily determined as 3 wt% of PAMSQs. Unexpectedly, among the PAMSQs, the highest heat differentiation was 24 mol% of PAMSQ (Fig. 1). In other words, PAMSQ-III had the most efficient mol fraction for photopolymerization. It could be explained that the whole acryloyl groups in molecule did not attend at once when radical was generated by photo-initiator because of solid state of materials.

To investigate a more effective photo-initiator the photopolymerization was carried out using Irgacure-784, a free radical titanosen compound. Comparing the heat differentiation of PAMSQ at 24 mol% with Irgacure-184, Irgacure-784 showed much lower efficiency than Irgacure-184 (Fig. 2).

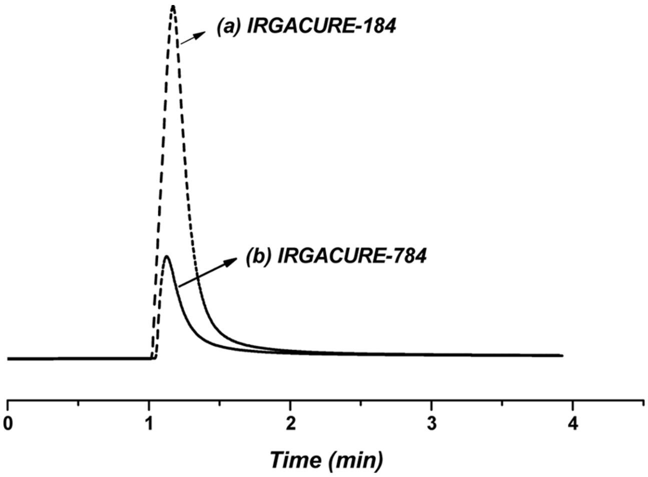

Figure 2. Photo-DSC curves of PAMSQ-III with (a) Irgacure-184 and (b) Irgacure-784.

Thermal Properties

Thermal stability is very important physical property of waveguide materials. Because of thermal deterioration, the thermal instability of materials exerts a bad influence in waveguide fabrication. This was prevented by the cross-linked Si–O–Si bond which had high decomposition temperature above 800°C. The decomposition temperature of the cross-linked polymer was also found to be higher than that of the initial polymer. It is the point that hydrolysate of TEOS reacted after copolymerization of trialkoxysilanes to increase the thermal stability of PAMSQs by inducing network structures.

The thermal decomposition behavior of PAMSQ-III was analyzed by TGA as shown in Figure 3. The initial decomposition was observed below 100°C by condensed water. It was demonstrated that the molecules had a chance to build more network structure from active hydroxyl groups. The thermal decomposition of PAMSQ slowly occurred from the acryloyl group in the range of 100∼400°C as well. However, after UV-curing of PAMSQ the second decomposition temperature increased from 350°C to 450°C due to the construction of more complex network structures by coupling of acryloyl groups. Finally, it was found that the most stable structure of PAMSQ was obtained by annealing and UV-curing.

Optical Properties

To measure the optical properties, the samples which were mixed with 3 wt% photoinitiator were annealed at 150°C for 10 minutes, and then exposed to UV irradiation for 10 minutes. The transverse electric (TE) and transverse magnetic (TM) refractive indices of the prepared films were measured by a prism coupler at 633 nm.

When acryl mol% in PAMSQ was increased, TE and TM refractive indices increased as shown in Figure 4. The birefringence (Δn), defined by the difference between in and out of plane refractive indices were also calculated. The birefringence

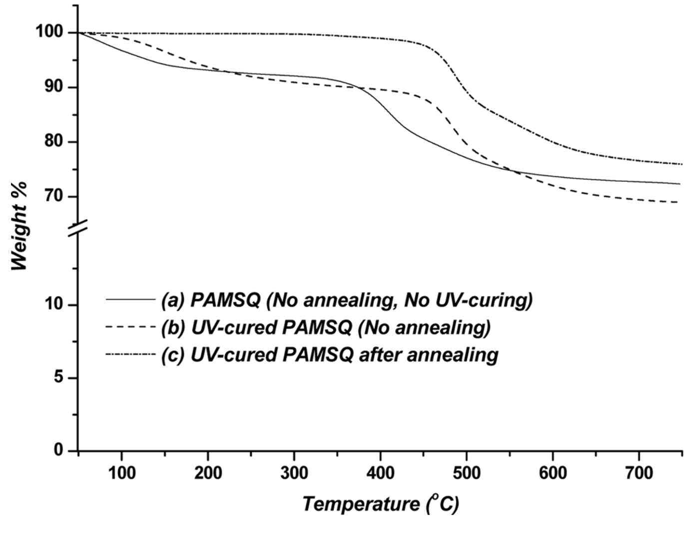

Figure 3. TGA curves of PAMSQ-III as curing method, (a) no annealing and no UV-curing, (b) UV-curing and no annealing and (c) UV-curing after annealing.

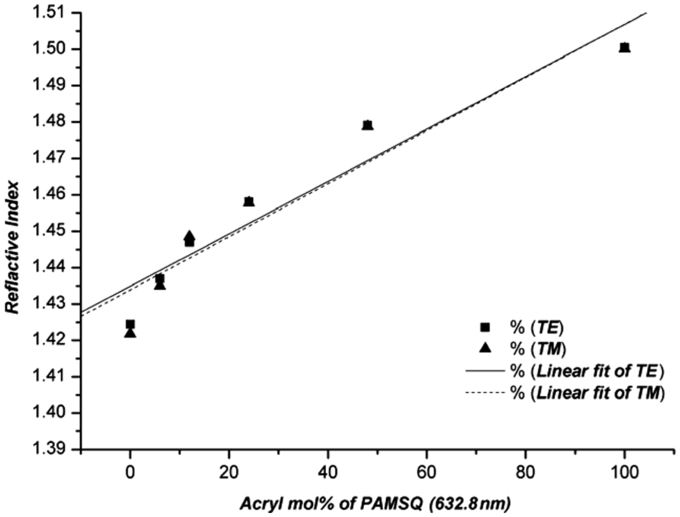

Figure 4. Refractive indices of PAMSQs at 633 nm.

of PAMSQ slowly decreases with increasing acryl group as Figure 5. The birefringence of PAMSQs was small, which fits with the conditions of waveguide materials.

Figure 6 shows the near-IR (NIR) spectra of PAMSQs in the wavelength range of 500~1800 nm. The NIR spectra give us important information. There are three main peaks around 1729, 1438, and 1176 nm. The peaks are assigned to the third harmonic of C–H bond stretching vibration ($3\nu_{C-H}$) in 1176 nm, the second harmonic of O–H bond stretching vibration ($2\nu_{O-H}$) in 1438 nm, and the second harmonic of C–H bond stretching vibration ($2\nu_{C-H}$) in 1729 nm. The optical losses of the planar waveguides were measured from coated thin films of PAMSQs, which are in the range of 0.005~0.02 dB/cm, smaller than those of corresponding PMMA planar waveguides [8].

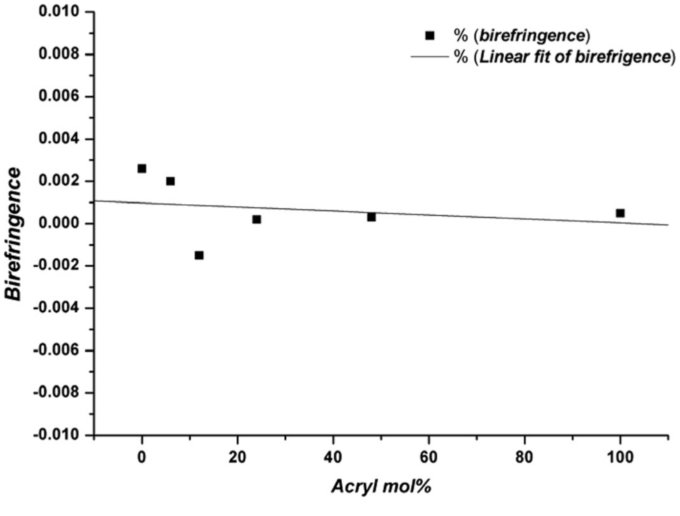

Figure 5. Birefringences of PAMSQs at 633 nm.

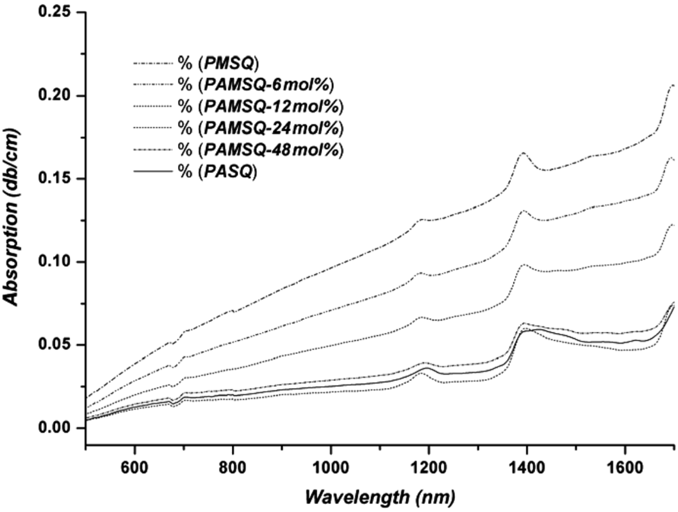

Figure 6. Near-IR spectra of PAMSQs.

Conclusion

PMSQs series with UV-curable group were prepared by hydrolysis and condensation reaction with water and acid. These polymers were become cross-linked by UV-irradiation and improved heat resistance by thermal processes. It was demonstrated by photo-DSC that PMSQ with 24 mol % acryl group had the best UV-curable condition. As refractive indices increased with increasing acryl mol%, the refractive index of PAMSQ could be controlled by the amount of acryloyl group. The optical losses were below 0.002 dB/cm in the absorptions at 830, 1330, and 1550 nm. Optical loss was independent of a varity molar ratio.

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