

Preparation and Characteristics of Cross-Linkable Polysulfone Having Methylene Methacrylate Side-Chain

Eun Sang Lee,^{1,2} Sung Kwon Hong,² Yong Seok Kim,¹ Jae Heung Lee,¹ Jong Chan Won¹

¹Advanced Materials Division, Korea Research Institute of Chemical Technology, 100 Jang-dong, Yuseong-gu, Daejeon 305-343, Korea

²Department of Polymer Science and Engineering, Chungnam National University, 220 Gung-dong, Yuseong-gu, Daejeon 305-764, Korea

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ABSTRACT: Polysulfone (PSF)s are amorphous polymers which possess excellent thermal stability and good optical properties. But they have drawbacks such as poor chemical resistance and high thermal expansion property. In this study, we introduced crosslinkable acrylic moiety in PSF with side-chain using chloromethylation method. We prepared photosensitive PSF having methylene methacrylate side-chain from chloromethylated polysulfone (CMPSF). And we performed solvent casting films of the polysulfone methylene methacrylate (PSFMM) and produced the cross-linked PSF films via UV expose. Their properties such as

the thermal, optical, gas barrier properties, and chemical resistance were measured by TGA, DSC, TMA, UV-transmittance, MOCON test, and solubility test. The crosslinked PSFMMs were insoluble in various protic and aprotic polar solvents. They have low CTE (coefficient of thermal expansion) value and gas barrier property improved according to increase of crosslinkable moiety. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1–8, 2008

Key words: chloromethylation; polysulfone; methacrylic acid; crosslinking; plastic substrate

INTRODUCTION

Technologies such as LCD, OLED are commonly used for the notebook monitor, display panel of cellular phone that are display substrates which need portability. The LCD and OLED have ability to express more light weight and thinner of the product, so it can be considered the appropriate technology of display substrate of mobile products. The glass substrate is commonly used for the display substrate. However, it has disadvantages which are heavy, easily fragile, and expensive to produce. So, there are many researches to reduce the thickness of glass substrates for more light weight and thinner for display substrate, but glass becomes easily fragile when it is thinner, so the fabrication process might be complicated and it results in the decrease of production rate.¹

Recently, there is a development of plastic substrates which are replaced with glass substrates as display substrates. Plastic substrates easily deal with

more light weight and thinner, and they also make possible to treat impact resistance, flexibility, and roll-to-roll process by their choice of plastics such as PET, PES, PC, and cyclic olefin copolymer (COC). So, they are practically adapted in the field of commercial part compared with glass substrates. They should have excellent transparency, high dimensional stability and low gas barrier property to use for the substrates of display.

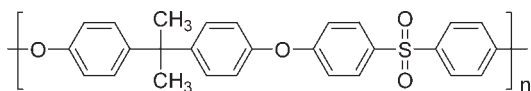
Other characteristics as well as chemical resistance are very crucially treated to be adapted as the substrates of display. The display substrate requires chemical resistance to avoid the damage of substrates because it is disclosed in the chemical process of module fabrication.

It is well known that PSF is amorphous polymer with a high glass transition temperature, good thermal and oxidative stability (decomposition range between 400 and 550°C regardless of environment—under air, argon, or vacuum), excellent strength and flexibility, resistance to extremes of pH values and low creep.^{2,3} But it is soluble in many organic solvent.

In this study, we effort the improvement of chemical resistant of PSF. We introduced crosslinkable side chain with acrylate. The introduction of side-chain acrylate improved chemical resistant without large deterioration of optical property and thermal properties. There is an interest in the chemical modification of the PSF especially by the halomethylation reaction^{1,4,5} leading to improved chemical resistance of the PSF. And we carry out UV-curing. The

Correspondence to: J. C. Won (jcwon@kriict.re.kr).

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Scheme 1 The structure of polysulfone.

UV-curable systems is notably demonstrated by the numerous studies published in this field over the past 15 years.^{6–14} The main reasons for this interest are the considerable advantages offered by the UV-curing process of polymerization over more conventional processes such as thermal curing, including very high speeds of curing that lead to high productivity, lower energy consumption, reduction of volatile organic compounds emissions, and so forth.⁶ Methacrylates of side chain are crosslinkable when exposed at UV radiation.

EXPERIMENTAL

Materials

The PSF (polysulfone) was used as a product of BASF (Ultrason S-2010) which has an average molecular weight around 60,000 and its polydispersity is 1.37 (by GPC, polystyrene standard) with the repeating unit as shown in Scheme 1. It was purified by dissolution in chloroform, precipitation with methanol and finally dried in vacuum oven at 40°C for 24 h. Chloroform above purity 99% with moisture content 30 ppm was purchased from Junsei Chemical. *N,N*-dimethylformamide (DMF) above purity, 99.9%, was purchased from Sigma-Aldrich. *N,N*-dimethyl acetamide (DMAc) above purity 99% with moisture content control under 30 ppm was purchased from Mitsubishi Gas Chemical Ind. Paraformaldehyde (95%; Aldrich), chlorotrimethylsilane (99+%; Aldrich), tin(IV) chloride (99%; Aldrich), methacrylic acid (99%; TCI), tetra-*n*-butylammonium bromide (TBAB, 99%; Aldrich), and potassium carbonate (K₂CO₃, 99+%; Aldrich) were used without purification.

Measurements

The coefficient of thermal expansion (CTE) was measured in the extension mode using a thermo-mechanical analyzer (TMA) (TA Instruments, model 2940). FTIR spectra were determined by Bio-Rad Digilab Division FTS-165 spectrometer. Haze and UV spectra were investigated by Prism Coupler SPA-4000 and Hewlett-Packard 8453 for measuring of optical properties, respectively. The ¹H NMR spectra were recorded on Bruker AMX-300 MHz spectrometer with CDCl₃. The water vapor permeation property were recorded on MOCON (Permatran

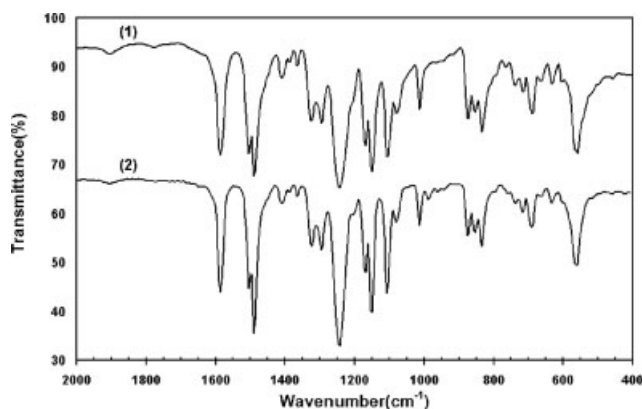


Figure 1 FTIR spectra of (1) PSF and (2) CMPSF9.

W3/31). Thermal properties were measured on thermogravimetric analysis (TGA) by TA Instrument TGA Q500 and differential scanning calorimetry (DSC) analysis by TA Instrument DSC Q1000 at heating rate of 10°C/min under nitrogen flow up to 800, 250°C, respectively.

Synthesis of PSF with side-chain

Chloromethylation of polysulfone (CMPSF)

PSF (5 g) dissolved in chloroform (165 mL) into a round bottom flask equipped with mechanical stirrer and thermometer. The solution was heated at 50°C under a nitrogen atmosphere, then paraformaldehyde (3.39 g), chlorotrimethylsilane (12.3 g), and

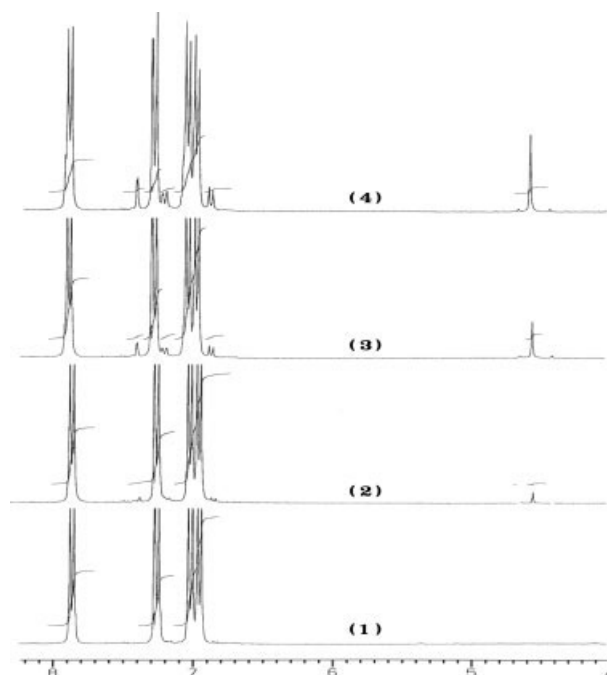


Figure 2 ¹H NMR spectra of (1) PSF, (2) CMPSF3, (3) CMPSF9, and (4) CMPSF18.

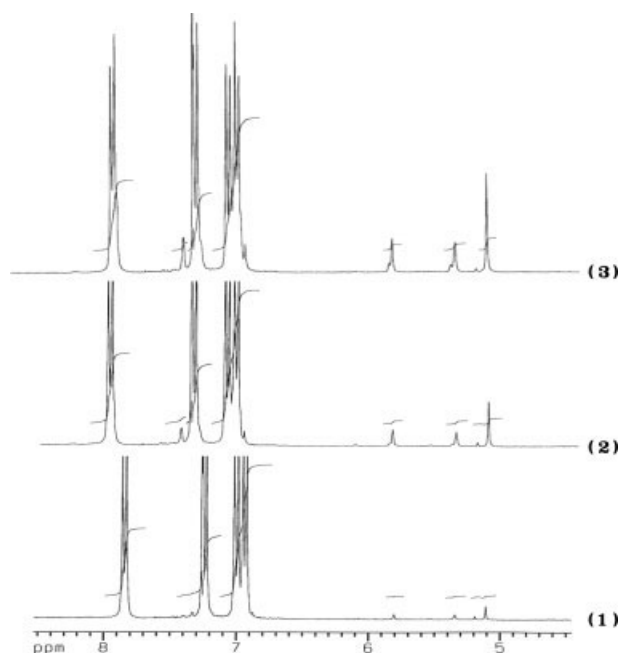
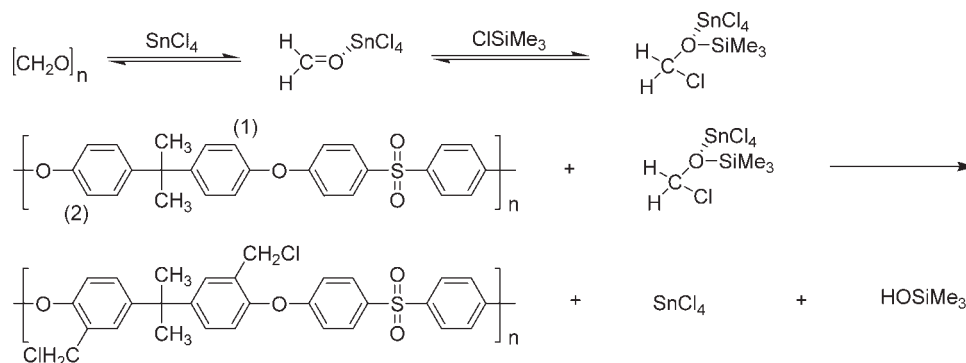


Figure 3 ^1H NMR spectra of (1) PSFMM3, (2) PSFMM9, and (3) PSFMM18.

tin(IV) chloride (0.589 g) for the catalyst added to a polymer solution. Once the reaction was completed, the mixture poured into methanol under stirring and the separated polymer precipitate filtered, then washed well with methanol, and finally dried in vacuum oven at 40°C for 24 h. The yield was obtained quantitatively.

The degree of substitution was influenced by the polymer concentration, the reaction time, the catalyst concentration, and the molar ratio of PSF repeating unit versus chloromethylation agent.^{1-4,15-17} So we could control the ratio of introduced $-\text{CH}_2\text{Cl}$ group with side chain in PSF. It was shown in FTIR spectrum in Figure 1 which presented to appear of $-\text{CH}_2$ rocking ($-\text{CH}_2\text{Cl}$) band at 990 cm^{-1} .

The amount of introduced $-\text{CH}_2\text{Cl}$ group was measured by ^1H NMR integration for 4.53(s, 4H) (Fig. 2).



Scheme 2 The chloromethylation reaction of polysulfone.

^1H NMR ($\text{CDCl}_3\text{-d}_6$, δ , ppm): 1.69(s, 6H), 4.53(s, 4H), 6.81–6.84(d, 1H), 6.92–6.94(m, 1H), 6.98–7.03(m, 4H), 7.14–7.15(m, 1H), 7.22–7.25(d, 2H), 7.35–7.36(d, 1H), 7.82–7.87(m, 4H).

CMPSF with methylene methacrylate

It was completely dissolved dimethylformamide (DMF, 50 mL) of CMPSF (2.5 g) and methacrylic acid (1.2 equivalent to $-\text{CH}_2\text{Cl}$), 1 equivalent (to $-\text{CH}_2\text{Cl}$) of K_2CO_3 and TBAB were added. The reaction mixture was stirred for 24 h at 40°C under a nitrogen atmosphere. After the reaction was completed, the mixture poured into distilled water under stirring and the separated polymer filtered, then severally washed well with distilled water, and finally dried in vacuum at 40°C for 24 h.¹⁸ The yield was obtained above 99% (Fig. 3).

^1H NMR ($\text{CDCl}_3\text{-d}_6$, δ , ppm): 1.74(s, 6H), 1.75(s, 6H), 5.11(s, 4H), 5.34(d, 2H), 5.80(d, 2H), 6.88–7.01(m, 6H), 7.20–7.26(m, 3H), 7.32–7.33(d, 1H), 7.81–7.86(m, 4H).

Film casting

We prepared two groups of polymer solution. One group was PSFMM and the other group was blended PSF and PSFMM 18 (PSFMMb). PSFMM completely dissolved in DMAc for 10 wt % of the solid content. The PSFMM solution was casting on the glass plate by the Doctor's blade. It was cured by UV exposure for 4.5 J/cm^2 . And then, it dried in vacuum oven at 60°C for 30 min, 120°C 1 h, and 150°C for 24 h.

RESULTS AND DISCUSSION

Synthesis and characterization of CMPSF

The chloromethylation reaction occurred according to Scheme 2. The chloromethylation was the replacement of a hydrogen atom in an aromatic compound

TABLE I
The Relation of Reaction Time with Degree of Substitution

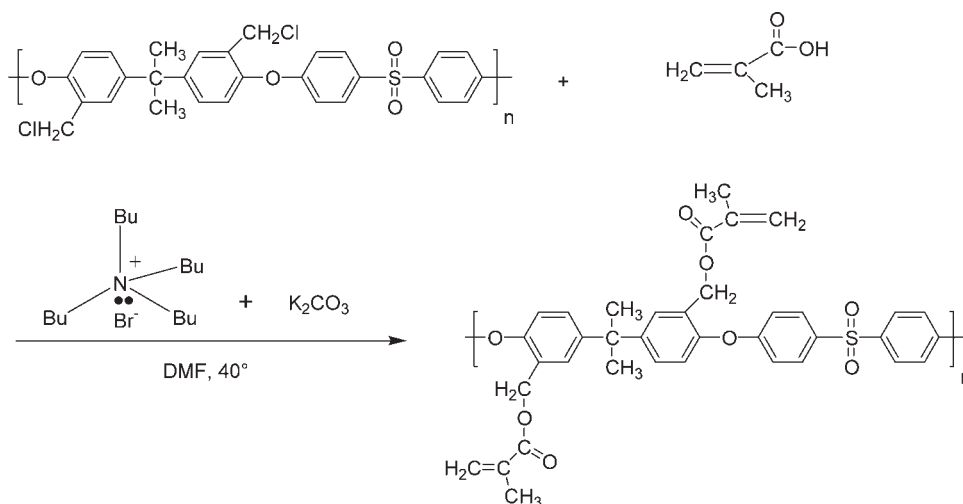
Polymer code	Reaction time (h)	Degree of substitution (per repeating unit)
PSF	0	0
CMPSF3	10	0.06
CMPSF9	15	0.18
CMPSF18	24	0.36

by a chloromethyl group. PSF was reacted with chloromethyl group in presence of tin(IV) chloride as a catalyst, and this could be led to successful introduction of a chloromethyl group into the PSF. For the PSF, chloromethylation reaction occurred on the bisphenol-A group. Substitution of $-\text{CH}_2\text{Cl}$ group for hydrogen atom first took place on the position (1) (mono-substituted product), and then on the position (2) (di-substituted product).¹⁵ After the chloromethylation reaction we introduced UV-curable moiety which could be crosslinking, it was very important that the products were soluble in aprotic polar solvents such as DMSO, DMAc, DMF, THF, and NMP, and protic polar solvent like CHCl_3 .

The $-\text{CH}_2$ rocking vibration band of $-\text{CH}_2\text{Cl}$ was observed in FTIR spectrum at 990 cm^{-1} (Fig. 1). In ^1H NMR spectra of the resulting products, there represented a new singlet peak at 4.53 ppm, and this indicated proton of the $-\text{CH}_2\text{Cl}$. The integration ratio of the $-\text{CH}_2\text{Cl}$ proton peak increases with an increase in the degree of substitution, as shown in Figure 2.

It could calculate using the following equation for the degree of substitution (DS):

$$\text{DS} = \frac{B/4}{A/6} \times 100$$



Scheme 3 The reaction of chloromethylated polysulfone with methacrylic acid.

where, A is the integration of the $-\text{CH}_2\text{Cl}$ proton, B is the integration of the $-\text{CH}_3$ proton on the bisphenol-a unit.

In this study, we controlled the reaction time. And the characteristics of studies for CMPSFs are given in Table I.

The reaction of CMPSF with methacrylic acid

To attempt synthesis of photosensitive PSF, we explored the esterification of CMPSF with methacrylic acid,^{19–21} that occurs according to Scheme 3. The reaction was performed in the presence of K_2CO_3 as a reaction catalyst and TBAB as a phase-transfer catalyst. From the ^1H NMR spectrum of the resulting product, all of the peaks according to the $-\text{CH}_2\text{Cl}$ proton disappeared, and the new peaks for the methacrylic acid proton appeared. It was identified that the reaction was complete. The peak integration was increased according to the amount of $-\text{CH}_2\text{Cl}$ proton which was shown in Figure 2.

Characterizations of PSFMM

The $\text{C}=\text{C}$ double bonds were observed in FTIR spectroscopy at 1637 cm^{-1} . It exposed the UV intensities of 0.9, 2.9, 4.5, and 18 J/cm^2 . The case of PSFMM9 which was exposed the UV below 4.5 J/cm^2 was rapidly the decrease of $\text{C}=\text{C}$ double bond and above 4.5 J/cm^2 was retained the $\text{C}=\text{C}$ double bond, as shown in Figures 4 and 5. The residue percentage of the $\text{C}=\text{C}$ double bond is calculated by

$$R(\%) = \frac{a}{b} \times 100$$

where, R is the residue percent of the $\text{C}=\text{C}$ double bond, a is the remains of $\text{C}=\text{C}$ double bond after

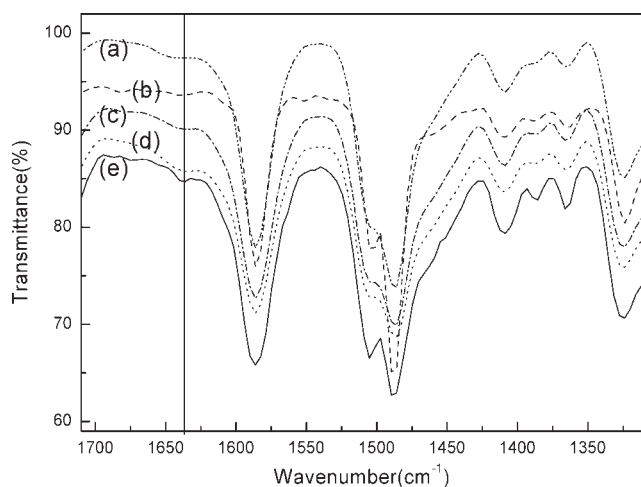


Figure 4 FTIR spectra of polysulfone methylene methacrylates with UV exposure strength. (a) PSFMM9, (b) 0.9 J/cm², (c) 2.9 J/cm², (d) 4.5 J/cm², and (e) 18 J/cm².

expose the UV, *b* is the C=C double bond of the PSFMMs.

After expose of the UV, it analyzed the each sample with FTIR spectrometer. The remains of C=C double bond in PSFMM series are given in Table II. The result of C=C double bond analysis, we fixed expose of 4.5 J/cm² for PSFMM series.

Optical properties

For use of plastic display substrate, matrix sheet should have good transparency. Because polysulfone is an amorphous polymer, it represents excellent transparency. So the PSFMM also should be amorphous polymer and transparency. In this study, we had casting of the PSFMM films, and measured optical properties such as the haze, the UV-transmittance, and the yellow index (YI). We compared the

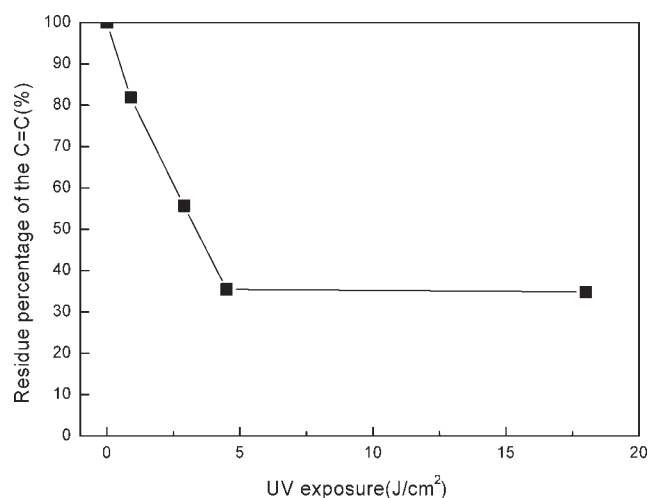


Figure 5 The relations of the residue percentage of the C=C bond according to the amount of UV exposure.

TABLE II
The Residual Percentages of the C=C bond of PSFMM Series after UV Exposure

Polymer code	Residual C=C bond (%)
PSFMM3	96
PSFMMb3	59
PSFMM9	35
PSFMMb9	33
PSFMM18	38

PSFMM films with the PSF film. After completely removing the solvent of the PSFMM film, retain the transparency. The results of optical property measurements for PSF and PSFMM films were shown in Table III. As the degree of side-chain acrylate of PSFMMs were increased, UV transmittance and YI, haze characteristics were a little bit decreased. But it was a range that we could use it as a display substrate.

Chemical resistance

The solubility of crosslinked PSFMMs were measured into various protic and aprotic polar solvents such as CHCl₃, DMAc, DMF, NMP, THF, isopropyl alcohol, acetone, γ -butyrolactone, HCl, HNO₃. The result of solubility test; the PSF film was soluble in solvents, but the PSFMM3 film was partially soluble in CHCl₃ but insoluble in others solvents, and the others were insoluble in various solvents, as shown in Table IV. It is explained by chemical properties of the thermosetting polymer by crosslinking. The thermosetting polymers are insoluble in most solvents. As a result, the crosslinked PSF by the photosensitive moiety was not soluble in solvents. While crosslinked PSF is used for display substrate, it should be insoluble in isopropyl alcohol, acetone, *N*-methyl pyrrolidone, γ -butyrolactone, HCl, and HNO₃ solvent that are widely used in the device fabrication process, as shown in Table IV.

Thermal properties by TGA, DSC, and TMA

Thermogravimetric analysis data of PSF and PSFMM were presented in Table V and selected TGA traces

TABLE III
The Optical Properties of PSF and PSFMM Series

Polymer code	Haze (%)	YI	Transmittance (%)	
			550 nm	700 nm
PSF	0.27	0.38	92.3	93.1
PSFMM3	0.35	0.40	88.9	92.0
PSFMMb3	0.32	0.39	88.3	91.2
PSFMM9	0.46	0.41	88.2	90.1
PSFMMb9	0.41	0.42	88.4	90.7
PSFMM18	0.52	0.45	88.0	90.1

TABLE IV
The Solubility Tests of PSF and PSFMM Series

Solvent	Polymer code					
	PSF	PSFMM3	PSFMMb3	PSFMMb9	PSFMM9	PSFMM18
CHCl ₃	++	Δ	Δ	Δ	--	--
DMAc	++	Δ	Δ	Δ	--	--
DMF	++	Δ	Δ	Δ	--	--
NMP	++	Δ	Δ	Δ	--	--
THF	++	Δ	Δ	Δ	--	--
Isopropyl alcohol	--	--	--	--	--	--
Acetone	--	--	--	--	--	--
γ-butyrolactone	--	Δ	Δ	Δ	--	--
HCl (1 mol/L)	--	--	--	--	--	--
HNO ₃ (60 %)	--	--	--	--	--	--

++ : soluble at room temperature, Δ : partially-soluble at room temperature, -- : insoluble.

were presented in Figure 6. The temperature of weight loss before 480°C was generally considered to be the decomposition temperature of the cross-linkable moiety which was increased according to the amount of methacrylate moiety. The side-chain moiety weakens to compare with the main-chain that its degradation point represents to happen at low temperature. But it is not important because degradation points of crosslinked PSFs were higher than that of display fabrication processing temperature (250–300°C).

The representative DSC thermograms had been plotted in Figure 7 for crosslinked PSF. As they can be seen from Figure 7, the glass transition temperature of the PSF ranged at 188°C. In case of crosslinked PSFMM3 T_g ranged to 195°C and the T_g of the PSFMM9 and PSFMM18 were increased to 210°C. The methacrylic moiety was rolled on network structure between PSFMM. The crosslinked parts disrupt movement of the each main chain. But some samples represented T_g because we introduced crosslinkable moiety partially in PSF in which permitted chain movement by main chain.

Most of polymeric materials increase volume with increasing temperature. It is called the thermal expansion. The degree of thermal expansion represents coefficient of thermal expansion (CTE). The

measurement of CTE has a couple of methods, one is the linear expansion for the thermal, the other is the volume expansion for the thermal. The former called the coefficient of linear expansion and the latter called the coefficient of volume expansion. In this study, we measured the coefficient of linear expansion for the CTE by TMA.

It could be calculated using the following equation for the CTE (a):

$$a = \frac{1}{L_0} \times \frac{L_2 - L_1}{t_2 - t_1}$$

where, L_0 is the length of sample for 0°C, L_1 is the length of sample for T_1 °C, L_2 is the length of sample for T_2 °C, T_1 and T_2 are transformation of temperature for sample.

It demands the dimensional stability on the high temperature for the display substrate. We measured the CTE of the PSF and PSFMM films, as shown in Figure 8. The CTE was decreased with increasing of the degree of substitution. It was owing to chemical structure, the crosslinked moiety interrupt thermal expansion between main chains. The crosslinking effect at CTE was not obviously appeared samples between PSFMM9 and PSFMM18. So we will be

TABLE V
Thermogravimetric Analysis of PSF and PSFMM Series

Polymer code	IDT (°C)	T_d (°C)	T_5 (°C) ^a	T_{10} (°C) ^b	Residue (%)
PSF	472	512	500.6	509.5	31.7
PSFMM3	391	431	472.3	495.4	32.6
PSFMMb3	388	433	475.3	496.3	35.6
PSFMM9	387	430	432.9	474.2	32.9
PSFMMb9	382	432	428.4	470.5	35.4
PSFMM18	379	430	406.4	436.2	32.3

^a T_5 ; 5% weight loss temperature.

^b T_{10} ; 10% weight loss temperature.

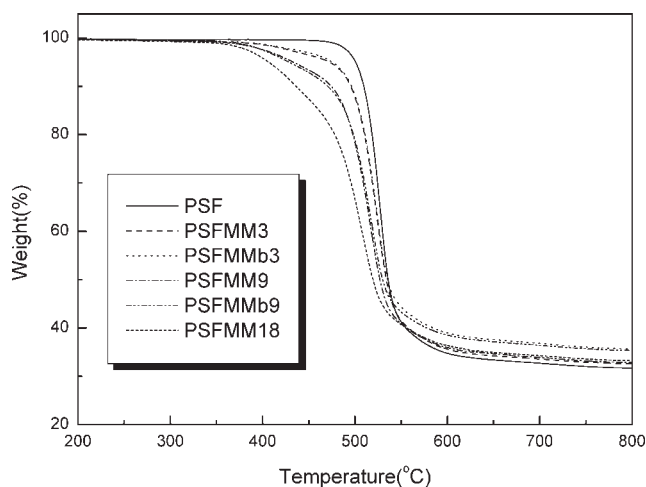


Figure 6 Thermogravimetric analysis of PSF and PSFMM series.

investigating this matter in future. But we can see the evidence of increase of degree of crosslinked moiety in PSFMM 18 by decreasing water vapor transmission ratio (WVTR).

Gas barrier property

The water vapor transmission ratio (WVTR) of the PSF and PSFMM films were measured by the conditions of 37.8°C, 100% humidities, as shown in Table VI. Crosslinked PSF films were decreased, WVTR, compare with the PSF film, because crosslinking decreased the free volume of polymer matrix which made denser structure of matrix. The water barrier property is calculated by barrier improvement factor (BIF). The increase of crosslinked moieties reduced water vapor permeability of matrix film. In case of PSFMM18, BIF value represents to 1.92.

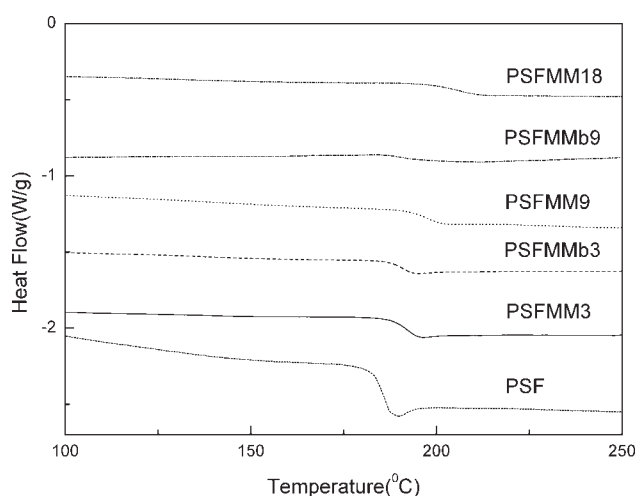


Figure 7 DSC thermograms of PSF and PSFMM series.

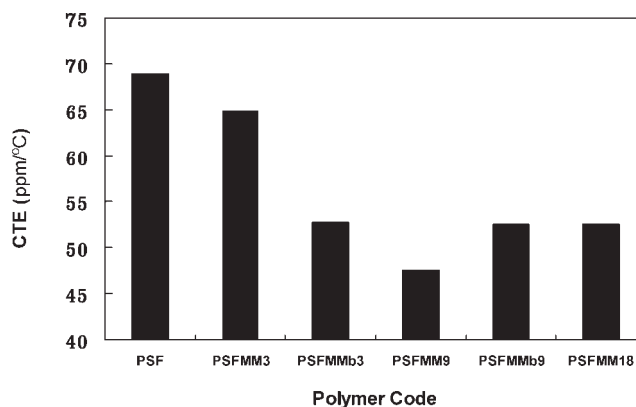


Figure 8 The coefficient of thermal expansion (CTE) of PSF and PSFMM series.

$$\text{BIF} = \frac{a}{b}$$

where a is water vapor transmission ratio of PSF, b is water vapor transmission ratio of PSFMMs.

CONCLUSIONS

We successfully introduced crosslinkable side-chain moiety in polysulfone by chloromethylation method. The UV curable polysulfones having methylene methacrylate with side-chain were prepared films by solvent casting. We controlled the degree of chloromethylation by the polysulfone concentration, reaction time, and catalyst concentration. The reaction time was important factor of degree of chloromethylation. The introduction of side-chain acrylate improved chemical resistant without large deterioration of optical property and thermal properties.

The PSFMM films above 9% for degree of substitution were insoluble in various organic solvents. They were insoluble in various protic, aprotic polar solvent, and acid-base.

The PSFMM films represented low CTE (coefficient of thermal expansion) value which decreased

TABLE VI
The Water Vapor Permeabilities of PSF and PSFMM Series

Polymer code	Thickness of film (μm)	WVTR ($\text{g}/\text{m}^2 \text{ day}$)	BIF
PSF	86.2	102	1
PSFMM3	74.9	84	1.21
PSFMMb3	82.3	76	1.34
PSFMM9	83.6	67	1.52
PSFMMb9	84.4	65	1.57
PSFMM18	80.3	53	1.92

Measurement conditions; temperature: 37.8°C, humidity: 100%.

to 25%. In addition, they represented improved gas barrier property. The barrier improvement factor (BIF) of PSFMM18 film was above 1.92.

References

1. Warshawsky, A.; Kahana, N.; Deshe, A.; Gottlieb, H. E.; Arad-yellin, R. *J Polym Sci Part A: Polym Chem* 1990, 28, 2885.
2. Avram, E.; Brebu, M. A.; Warshawsky, A.; Vasile, C. *Polym Degrad Stabil* 2000, 69, 175.
3. Ma, S. L.; Kim, Y. S.; Lee, J. H.; Kim, J. S.; Kim, I. S.; Won, J. C. *Polymer (Korea)* 2005, 29, 204.
4. Avram, E.; Butuc, E.; Luca, C.; Druta, I. J. *Macromol Sci Pure Appl Chem* 1997, A34, 1701.
5. Vasile, C.; Elena, B.; Avram, E.; Airinei, A. *Appl Organomet Chem* 2003, 17, 282.
6. Avram, E.; Rusu, E.; Airinei, A. *Rev Roum Chim* 1998, 43, 765.
7. Vasile, C.; Avram, E. *Eur Polym Mater* 2003, 39, 107.
8. Zhang, A.; Li, X.; Nah, C.; Hwang, K. J.; Lee, M.-H. *J Polym Sci Part A: Polym Chem* 2003, 41, 22.
9. Daly, W. H. *J Macromol Sci Chem* 1985, A22, 713.
10. Timmer, M. D.; Ambrose, C. G.; Mikos, A. G. *J Biomed Mater Res A* 2003, 66, 811.
11. Pavlinec, J.; Moszner, N. *Macromol Mater Eng* 2003, 288, 789.
12. Deb, S.; Vazquez, B.; Bonfield, W. J. *Biomed Mater Res* 1997, 37, 465.
13. Barbeau, P. H.; Gerard, J. F.; Magny, B.; Pascault, J. P. *J Polym Sci Part B: Polym Phys* 2000, 38, 2750.
14. Lin, S. B.; Tsay, S. Y.; Speckhard, T. A.; Hwang, K. K. S.; Jezerc, J. J.; Cooper, S. L. *Chem Eng Commun* 1984, 30, 251.
15. Koshiba, M.; Hwang, K. K. S.; Foley, S. K.; Yarusso, D. J.; Cooper, S. L. *J Mater Sci* 1982, 17, 1447.
16. Speckhard, T. A.; Hwang, K. K. S.; Lim, S. B.; Tsay, S. Y.; Koshiba, M.; Ding, Y. S.; Cooper, S. L. *J Appl Polym Sci* 1985, 30, 647.
17. Lai, Y.-C.; Baccei, L. J. *J Appl Polym Sci* 1991, 42, 2039.
18. Kim, H. D.; Kang, S. G.; Ha, C. S. *J Appl Polym Sci* 1992, 46, 1339.
19. Kim, B. K.; Lee, K. H.; Kim, H. D. *J Appl Polym Sci* 1996, 60, 799.
20. Nabeth, B.; Gerard, J. F.; Pascault, J. P. *J Appl Polym Sci* 1996, 60, 2113.
21. Velankar, S.; Pazos, J.; Cooper, S. L. *J Appl Polym Sci* 1996, 62, 1361.