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Thermal stability of sol–gel derived methacrylate oligosiloxane-based hybrids for LED encapsulants

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Abstract Methacrylate oligosiloxane-based hybrid materials (methacrylate hybrimers) were fabricated by curing the methacrylate oligosiloxane resins synthesized by sol–gel condensation reaction of 3-(trimethoxysilyl)propyl methacrylate (MPTS) and diphenylsilanediol (DPSD) for the LED encapsulant application. The fabricated hybrimers are optically transparent and have a high refractive index up to 1.565 depending on the precursor composition. The lower DPSD content hybrimer, which is the more polymerized and heated in a vacuum to remove the non-polymerized methacrylate groups, produces higher optical transmittance and thermal stability. This behavior is interpreted by thermal degradation of methacylate groups in the hybrimers.

Keywords Photopolymerization · Polysiloxanes · Refractive index · Thermal properties · Transparency

1 Introduction

Light emitting diodes (LEDs) have received a great deal of attention for lighting in industries and research because of their energy efficiency and durability. Thus, LEDs are expected to be the most powerful candidate for lighting sources in the near future. The research on enhancing the light efficiency of white LEDs is the key issue in the development for LED lighting [1–4].

There are three packaging types of LEDs to illuminate white light by combining the LED chip and the phosphor inside the encapsulation. The first type uses a blue LED chip with yellow phosphor mixed in the encapsulation resin. The second one combines red, green and blue LED chips in a single packaging. Another uses a UV LED chip which is packaged with red, green and blue phosphors in the encapsulation resin. Thus, generally, the encapsulation resin mixed with the phosphors is used to yield white light as well as to protect the LED chip.

It is required for the encapsulants to have excellent transparency in the visible region, and heat, moisture, solvent and chemical resistance. In particular, since radiation of heat from an LED chip increases the temperature of an LED package, the encapsulants should be resistive to high temperatures. The heat during operation causes discoloration of the encapsulants, decreasing light efficiency. Thus, an essential property is to have excellent thermal stability against high temperatures to maintain the initial high brightness of LED light [5]. Also, a higher refractive index of the resin is desirable for efficient light extraction since the refractive index of an LED chip is typically over 2.0 [6, 7].

Recently, the sol–gel derived oligosiloxane-based hybrid materials (hybrimers) have been developed for many optical applications because they are very transparent and show relatively high thermal stability compared to typical polymers [8, 9]. Also, the refractive index can easily be increased by tailoring both compositions of organics and inorganics. The high transparency and high refractive index, as well as the improved thermal stability, can make the hybrimers usable as an LED encapsulation resin. We have fabricated the methacrylate hybrimer based on methacylate oligosiloxane synthesized by sol–gel condensation of 3-(trimethoxysilyl)propyl methacrylate (MPTS)

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and diphenylsilanediol (DPSD) for optical applications. The yellowing behavior of the methacrylate hybrimer depending on the precursor composition was examined to discuss the thermal stability of the hybrimer to be applied for the LED encapsulant.

2 Experimental

2.1 Synthesis of methacrylate oligosiloxane resins

The methacrylate oligosiloxane resins were synthesized by a sol–gel condensation process between 3-(trimethoxysilyl)propyl methacrylate (MPTS) and diphenylsilanediol (DPSD) with different compositions of precursor molar ratios from 33 to 55 mol% DPSD over MPTS (Table 1). As illustrated in Fig. 1, barium hydroxide monohydrate, $Ba(OH)_2 \cdot H_2O$ (BH, Aldrich, USA) was added as a catalyst to promote the direct condensation reaction of the methoxy radical of MPTS and the diol radical of DPSD to form siloxane bonds. This synthesis proceeded without the addition of water for hydrolysis, which can reduce the residual silanol contents [10].

The amount of BH was 0.1 mol% of the total silane compound. BH was used as a catalyst to activate the nucleophillic attack of silanol, but not to change the pH of the solution. Because BH does not dissolve in solvents or water, a neutral condition is preserved during reaction. The condensation process by BH catalyst of sol–gel method promotes condensation of precursors fast and results in

Table 1 Compositions of chemical precursors for synthesis of methacrylate oligosiloxane

Samples	MPTS (g)	DPSD (g)	$Ba(OH)_2 \cdot H_2O$ (g)	Mol% of DPSD
MD33	16.64	7.14	0.0189	33.3
MD41	14.48	9.02	0.0189	41.7
MD50	12.42	10.82	0.0189	50
MD55	11.18	11.90	0.0189	55
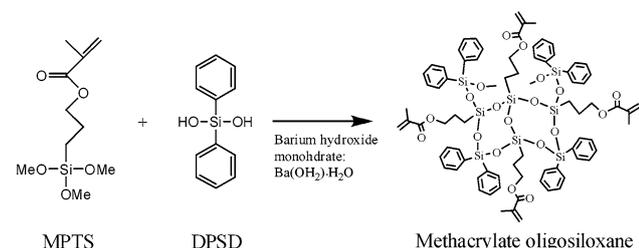
**Fig. 1** Synthesis of metacrylate oligosiloxane resin by sol–gel condensation reaction of MPTS and DPSD

highly branched clusters [11, 12]. Although BH is insoluble in water and any alcohol, it can be removed by filtering after the reaction. MPTS and BH were mixed in a flask, and DPSD was added continuously for 2 h during reaction. After adding DPSD to the solution, an additional 2 h reaction proceeded to complete the condensation reaction. The solution was stirred with a magnetic stirrer during reaction, which was performed at 80 °C. After the reaction, a by-product, methanol, was removed by vacuum heating. Also BH was removed by a using 0.45 μm pore-sized teflon filter. After filtering, the photo-curable transparent methacrylate oligosiloxane resins were synthesized by using non-hydrolytic sol–gel method between two precursors with base catalyst [13, 14].

2.2 Fabrication of methacrylate hybrimers for LED encapsulants

2, 2-dimethoxy-2-phenyl-acetophenone (BDK, Aldrich) was added as a photo-initiator for the photopolymerization of the methacrylate groups in the oligosiloxane resin. The BDK was added as 10 mol% of the total polymerizable methacrylate group with each different composition of methacrylate oligosiloxane. The synthesized methacrylate oligosiloxane resins were photo-cured to fabricate methacrylate hybrimers as other methacrylate polymers were. The resins were cast into a glass mold which consisted of two glasses separated by 2 mm. The resultant molds were illuminated by radiation from an ultraviolet (UV) lamp (500 W Hg Lamp, ∼ 365 nm, Oriel 97453) in N_2 atmosphere for 3 min. After the photo-curing, the 2 mm thick and uniform hybrimer plates were fabricated [15]. Then, the plates were separated by two groups. One group was heat-treated at 150 °C in air for 2 h, and the other group was heat-treated in a vacuum for the same period. The heat-treatment was performed to complete the curing and remove non-polymerized groups (Fig. 2).

2.3 Characterization of oligosiloxane resins and hybrimers

^{29}Si nuclear magnetic resonance (NMR) spectra of the oligosiloxane resins in 30 vol% of chloroform-d were recorded using a FT 600 MHz (Bruker Biospin DMX600) instrument. Chromium (III) acetylacetonate as a relaxation agent of silicon was added at a concentration of 30 mg/L. Solid-state ^{29}Si NMR spectra for the hybrimers were recorded using a FT 600 MHz NMR. (Varian INOVA^{unity}) Fourier transform-infrared (FT-IR) spectroscopy (JASCO, FT-IR 460 plus) was used for measuring the structural evolutions during the photopolymerization. All the measurements were performed with a resolution of 4 cm^{-1} in the wavenumber range 650–4,000 cm^{-1}. Transmittance
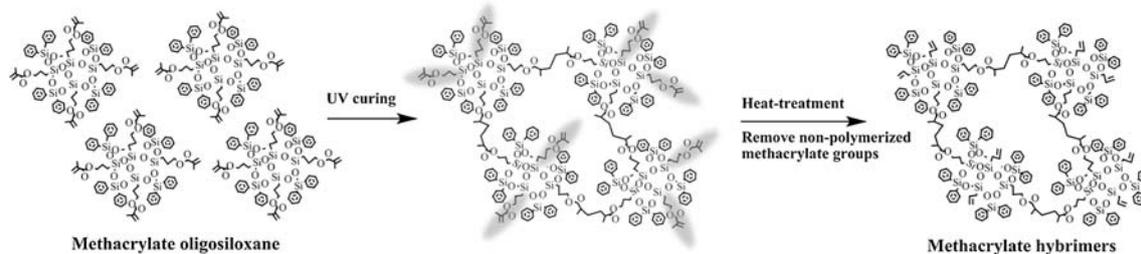
Fig. 2 Fabrication of methacrylate hybrimers by photo-curing and heat-treatment of synthesized resins

and yellowness indices of 2 mm thickness of hybrimers were measured by the UV/VIS/NIR spectrophotometer (Shimadzu, Kyoto, Japan, UV-3101PC). The measurement for yellowness indices of the hybrimers followed the ASTM Method D1925. A prism coupler (Pennington, Metricon 2010) was used to measure the refractive indices of the hybrimers at 633 nm, 25 °C.

3 Result and discussion

3.1 Formation of siloxanes in resins and hybrimers

Formation of siloxane bonds in the methacrylate oligosiloxane resins and hybrimers were confirmed by liquid state and solid state ^{29}Si NMR spectroscopy respectively as shown in Fig. 3. The notations of Si atoms in NMR spectroscopy are D^n and T^n which represent Si atoms from DPSD and MPTS, respectively.

A small peak at −29 ppm of the D^0 species due to diphenyldimethoxysilane is produced by reaction between DPSD and methanol. Only the MD55 composition has a small peak at −34 ppm which represents remaining DPSD in the resin. In the previous report of ^{29}Si NMR spectroscopy analysis, it was known that the increase of DPSD contents made the molecular size larger resulting in sterically blocking effect by more methacryl and phenyl groups to inhibit the condensation of DPSD [11].

Compared to NMR spectra of the resins (liquid state) and the hybrimers (solid state) in Fig. 3a, b, the relative peak assignments are almost identical. This represents the curing of the resins by photopolymerization, and heat-treatment in air does not significantly affect the siloxane formation. We calculated the degree of condensation of the resins and the hybrimers depending on the DPSD content in the reactants from NMR spectra using the following Eq. (1) [11].

$$DOC = \frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(T^0 + T^1 + T^2 + T^3)} \times 100$$

(1)

The more DPSD contents hybrimers have, the higher degree of condensation as shown in Table 2.

Since the attack of a nucleophilic deprotonated silanol from DPSD to MPTS increases as the portion of DPSD contents increases, the higher DPSD contained hybrimers have the higher siloxane bonds concentration which is combined with organic and inorganic units.

3.2 Photopolymerization of methacrylate oligosiloxane resins

In order to infer how much the photopolymerization was made in the methacrylate oligosiloxane resins depending on the DPSD content, the conversion degree of C=C bond in methacrylate was calculated through FT-IR spectra as shown in Fig. 4 using the following Eq. (2) [16].

Fig. 3 ^{29}Si NMR spectra of **a** methacrylate oligosiloxane resins (liquid state), **b** hybrimers (solid state)
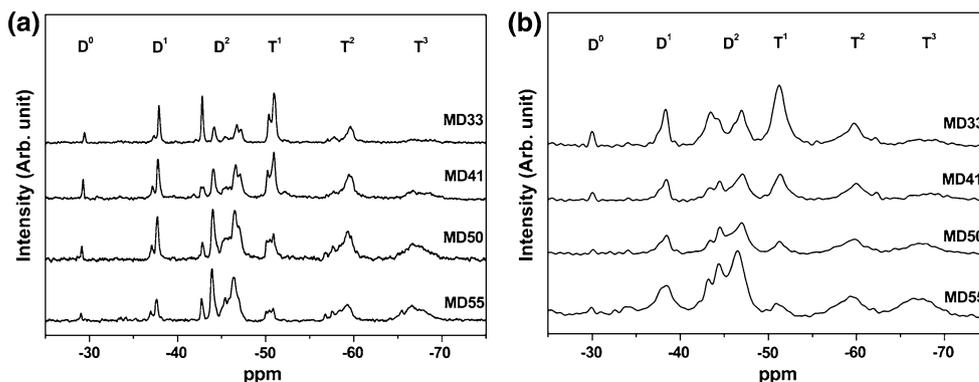
Table 2 Characteristics of methacrylate oligosiloxane and hybrimers

Sample	DOC (resin %)[a]	DOC (hybrimer %)[a]	Molecular weight (g/mol)	Estimated molecular structure	Conversion degree (%)	Refractive index
MD33	64.7	63.4	770	Tetramer	99.9	1.527
MD41	68.4	69.7	1,000	Pentamer	97.7	1.537
MD50	78.7	79.2	1,200	Hexamer	94.5	1.553
MD55	84.4	81.1	1,290	Hexamer	82.2	1.565

[a] *DOC* degree of condensation, refractive index measured at 633 nm, 25 °C
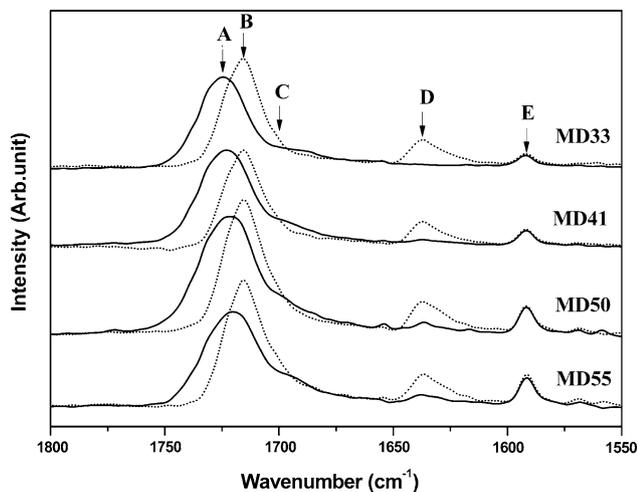
Fig. 4 FT-IR spectra of hybrimers for analysis of photo-curable behavior, where *A* shifted C=O in methacrylate group in hybrimer at 1,715–1,724 cm^{-1}, *B* C=O of methacrylate group in resin at 1,715 cm^{-1}, *C* C=O of hydrogen-bonded carbonyl group at 1,700 cm^{-1}, *D* C=C of methacrylate group at 1,638 cm^{-1}, *E* C=C of phenyl group at 1,590 cm^{-1} (*solid line*: hybrimer, *short dot line*: resin)

$$\text{Conversion degree}(\%) = \left[1 - \frac{\left(\frac{A_{C=C\,\text{in methacrylate group}}}{A_{C=C\,\text{in phenyl group}}} \right)_{\text{after UV}}}{\left(\frac{A_{C=C\,\text{in methacrylate group}}}{A_{C=C\,\text{in phenyl group}}} \right)_{\text{resin}}} \right] \times 100$$

(2)

$A_{C=C}$ in Eq. (2) represents the integrated peak intensities of the C=C in the methacrylate group (1,638 cm^{-1}) or phenyl group (1,590 cm^{-1}). The calculated conversion degrees depending on the composition are listed in Table 2.

The intensities of the peaks (D, in Fig. 4) from the double bonds (1,638 cm^{-1}) in methacrylate groups of MD33 and MD41 samples were removed completely after photopolymerization and heat-treatment. However, the double bond peaks at 1,638 cm^{-1} still remained in MD50 and MD55 samples even after photopolymerization and heat-treatment. This means complete polymerization was not made in the large DPSD content samples.

The peaks of C=O (B in Fig. 4) were shifted from 1,715 to 1,715–1,724 cm^{-1} (A in Fig. 4) after photopolymerization due to cross-linking with each molecular. As shown in Fig. 4, the C=O peaks of MD33 and MD41 which had high conversion degree of photopolymerization shifted from 1,715 cm^{-1} to around 1,724 cm^{-1} while the C=O peaks of MD50 and MD55 shifted from 1,715 cm^{-1} to approximately 1,721, 1,720 cm^{-1} respectively due to their insufficient photopolymerization by steric hindrance effect. The more the photopolymerized resins, the more the shift of the C=O groups. This shift by photopolymerization is typical for an ester carboxyl which is no more conjugated with a vinyl substituent [17].

The shoulder peaks at 1,700 cm^{-1} (C in Fig. 4) in the resin state represent C=O bonds of hydrogen-bonded carbonyl groups in the oligosiloxane resins. After photopolymerizaition and heat-treatment, these C=O bonds in methacrylate groups which are not polymerized remained more in the hybrimers as DPSD content increases in the hybrimers. This also represents that complete polymerization in MD50 and MD55 samples has not been made compared to MD33 and MD41.

In a previous report, it was revealed the molecular weight of the synthesized oligosiloxane grew from 770 to 1,290 as DPSD content increased from 33 to 55 mol%. While MD50 and MD55 samples with larger DPSD contents have mainly hexamer siloxane structure, major siloxane structures of MD33 and MD41 samples with lower DPSD contents were tetramer and pentamer siloxane structures. Thus, the larger molecular size in MD50 and MD55 samples interferes with photopolymerization due to steric hindrance effect. These non-polymerized methacrylate groups can be the source of the yellowing of hybrimers during aging.

3.3 Optical transparency and refractive index of methacrylate hybrimers

The fabricated plate samples (2 mm thickness) of the hybrimers with various DPSD compositions are very transparent in appearance. Light transmittances of the
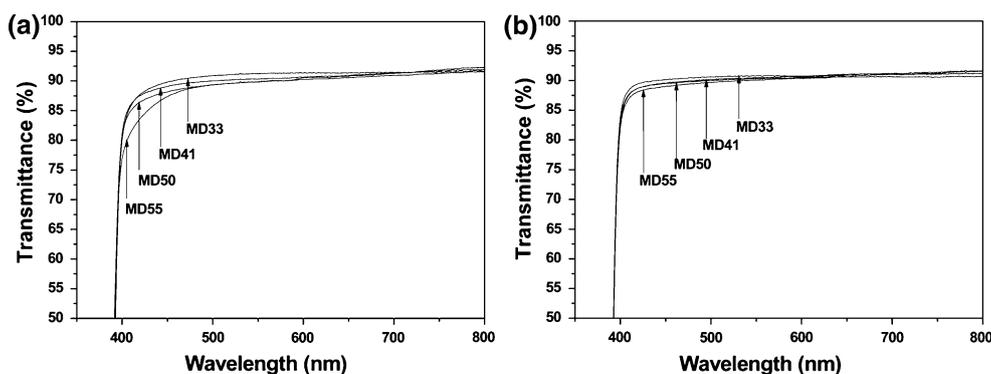
Fig. 5 Optical transmittances of different composition hybrimers which were heat-treated **a** in air and **b** in vacuum

samples which were measured by using the UV/VIS/NIR spectrophotometer were approximately 90% in the visible range. However, they are slightly dependent on the heating condition as well as the composition, as shown in Fig. 5.

First of all, the lower the DPSD content a hybrimer has, the higher the transmittance it shows among the samples heat-treated in air or vacuum. The more DPSD content a hybrimer contains, the larger sized oligosiloxane it produces, which makes the photopolymerization be prevented by steric hinderance effect. The lower cross-linking networks may decrease the transparency. Compared to the hybrimer heat-treated in air, the hybrimer heat-treated in a vacuum exhibits higher light transmittance. This is because the heat-treatment in a vacuum removes the non-polymerized methacrylate groups to make a dense network structure, as well as to remove decomposable species.

In addition, refractive indices of the samples were measured and listed in Table 2. The refractive index varies from 1.527 to 1.565 at a 633 nm (at room temperature) wavelength with changing the DPSD content from 33 to 55 mol% [18]. These values are higher compared to general silicone and methacrylate polymers. Usually, the refractive index of materials depends on electronic polarizability and density. The higher DPSD content sample with the more phenyl radicals which have high electronic polarizability shows the higher refractive index. Also, the more polymerization of the smaller sized oligosiloxanes

makes greater density in the lower DPSD content sample to increase the refractive index [19, 20].

### 3.4 Thermal yellowing of methacrylate hybrimers

The methacrylate group in the polymers is decomposed at higher temperature over 100 °C resulting in degradation of transmittance by yellowing the sample. The yellowness index of the sample as a function of temperature and time indicates thermal stability of the sample, which is the most significant characteristic for LED encapsulant application. In this study, after the hybrimer samples were aged at 150 °C in air for 72 h, the optical transmittances were measured as presented in Fig. 6.

Yellowness indices were calculated through the following Eq. (3) (ASTM, D1925), using the CIE tristimulus values of hybrimers which were measured by UV/VIS/NIR spectrophotometer.

$$YI(\text{Yellowness index}) = \left(\frac{1.28X_{CIE} - 1.06Z_{CIE}}{Y_{CIE}} \right) \times 100 \tag{3}$$

X_{CIE}, Y_{CIE} and Z_{CIE} in Eq. (3) represent the CIE tristimulus values for red, green and blue respectively. The changes of the transmittance (ΔT) at 450 nm and the yellowness index (ΔYI) before and after aging at 150 °C in air for 72 h are plotted in Fig. 7.

Fig. 6 Optical transmittances of hybrimers after aging at 150 °C in air for 72 h for the samples heat-treated in **a** air and **b** vacuum
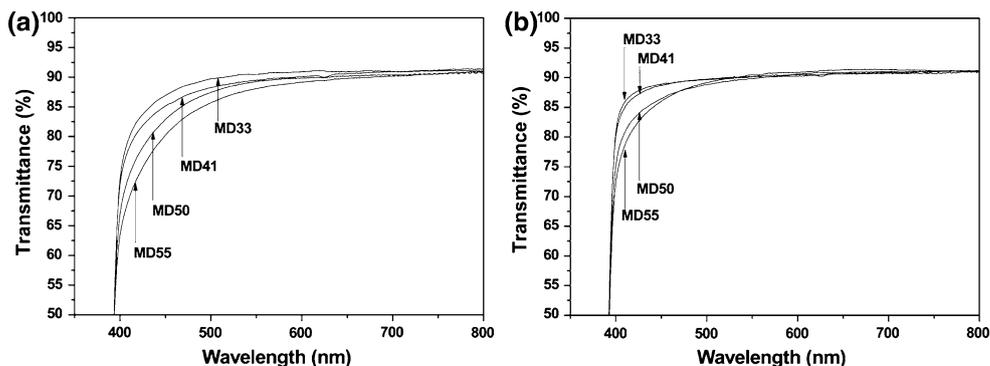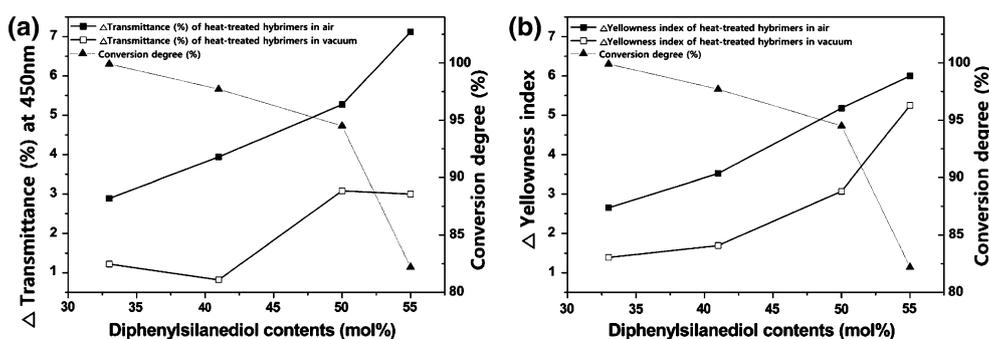
Fig. 7 **a** Changes in transmittance (ΔT) at 450 nm, **b** Change in yellowness index (ΔYI) of hybrimers with various DPSD contents after aging at 150 °C in air for 72 h

Fig. 8 Thermal degradation of non-polymerized methacrylate groups in hybrimers

Methacrylate group in methacrylate oligosiloxane   Alkene   Carboxylic acid
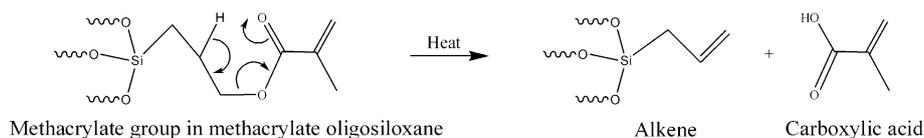
Generally, the samples heat-treated in a vacuum show lower ΔT and ΔYI than those heat-treated in air. Also, the samples with more DPSD contents exhibit the higher ΔT and ΔYI. This tendency is very similar to variation of optical transmittance depending on the composition and aging atmosphere. Thus, the MD33 sample with the smallest DPSD content is the most transparent and thermally stable. This is because it shows the higher conversion degree to contain the least non-polymerized methacrylate groups which can be the source of yellowing by thermal degradation. As shown Fig. 6, low conversion degree hybrimer represents that residual non-polymerized methacrylate groups still exist. And these residual groups result in yellowing after aging at high temperature. However, high conversion degree hybrimer shows good thermal stability even after aging at high temperature. Because almost all of the methacrylate groups are polymerized that means there are fewer yellowing sources than low conversion degree hybrimer.

As shown in Fig. 4, the shoulder peaks around at 1,700 cm^{-1} (C in Fig. 4) which represent C=O of hydrogen-bonded carbonyl groups in non-polymerized methacrylate groups [17]. This can cause yellowing of the hybrimer through thermal degradation. The mechanism for thermal degradation of carboxylic ester group in non-polymerized methacrylate group of hybrimer is shown as Fig. 8. This group undergoes a concerted elimination reaction to yield alkene and carboxylic acid [17, 21–25].

In contrast to non-polymerized methacrylate groups, the polymerized methacrylate groups are tightly cross-linked and connected with each molecule. This connection can hold molecules and prevent thermal degradation to cause yellowing.

4 Conclusions

Methacrylate oligosiloxane resins were synthesized by sol–gel condensation reaction of MPTS and DPSD with changing the precursor compositions. The resins were photopolymerized and heat-treated in air or vacuum to fabricated methacrylate hybrimers to be used as an LED encapsulant. The fabricated hybrimers show excellent optical transparency and high refractive index up to 1.565. Thermal stability over yellowing of the hybrimers was investigated by aging the samples at 150 °C in air for 72 h. The lower DPSD content samples heat-treated in a vacuum rather than in air exhibit the higher optical transmittances and the smaller changes in optical transmittances and yellowness indices. The more cross-linked network in the lower DPSD content sample and removal of non-polymerized methacrylate group by heating in vacuum lead the hybrimers to have better optical transparency and thermal stability. This behavior was explained and confirmed by FT-IR spectra of the hybrimer samples. Therefore, high refractive index and thermal stability over yellowing of the transparent methacrylate hybrimers are advantageous compared to other polymers to be applied for the LED encapsulant.

References

1. Huang JC, Chu YP, Wei M, Deanin RD (2004) Adv Polym Technol 23:298

2. Mohammad AK (1990) Electrical-optical devices and systems. PWS-KENT Publishing, Boston Chap.4
3. Rubinsztajn MI, Rubinsztajn S (2005) US Patent 6,916,889
4. Rubinsztajn MI, Rubinsztajn S (2006) US Patent 7,144,763
5. Narendran N, Gu Y, Freyssinier JP, Yu H, Deng L (2004) J Cryst Growth 268:449
6. Lester Steven D, et al. (1998) US Patent 577433
7. Taskar Nikhil R, et al. (2005) W.O. Patent 2005027576
8. Schubert U, Husing N, Lorenz A (1995) Chem Mater 7:2010
9. Watanabe T, Ooba N, Hayashida S, Kurihara T, Imamura S (1998) Lightwave Techol 16:1049
10. Buestrich R, Kahlenberg F, Popall M, Dannberg P, Müller-Fieldler R, Rösch OJ (2001) Sol-Gel Sci Technol 20:181
11. Eo YJ, Lee TH, Kim SY, Kang JK, Han YS, Bae BS (2005) J Polym Sci, Part B: Polym Phys 43:827–836
12. Stevens MP (1999) Polymer chemistry, 3rd edn. Oxford University Press, Oxford and New York, p 65
13. Streppel U, Dannberg P, Wächter C, Bräuer A, Fröhlich L, Houbertz R, Popall M (2002) Opt Mater 21:475
14. Buestrich R, Kahlenberg F, Popall M, Martin A, Rösch O (2000) Mater Res Soc Symp Proc 628, Warrendale, p CC9.8.1
15. Allcock HR, Lamp FW, Mark JE (2003) Contemporary Polymer Chemistry. New Jersey, third edition (Person Education, Inc., p 649
16. Kim WS, Houbertz R, Lee TH, Bae BS (2004) J Polym Sci, Part B: Polym Phys 42:1979
17. Saravanamuttu K, Du XM, Najafi SI, Andrews MP (1998) Can J Chem 76:1717
18. Eo YJ, Kim JH, Ko JH, Bae BS (2005) J Mater Res 20:401
19. Kang ES, Park JU, Bae BS (2003) J Mater Res 18:1889
20. Park OH, Seo SY, Jung JI, Bae JY, Bae BS (2003) J Mater Res 18:1039
21. Jäger K-M, Dammert RC, Sultan B-Å (2002) J Appl Polym Sci 84:1465
22. Cervantes-Uc JM, Cauich-Rodíguez JV, Vázquez-Torres H, Licea-Claveríe A (2006) Polym Degrad Stab 91:3312
23. Li X, King TA (1996) J Non-Cryst Solids 204:235
24. Rao CNR (1963) Chemical applications of infrared spectroscopy. Academic Press, New York, p 24
25. Coltrain BK, Landry CJT, O'Reilly JM, Chamberlain AM, Rakes GA, Sedita JS, Kelts LW, Landry MR, Long VK (1993) Chem Mater 5:1445