

## An UV-curable epoxy acrylate oligomer with high refractive index containing fluorene: Preparation, characterization, and application

Jia Chen,<sup>1</sup> Yuming Zhou,<sup>1</sup> Qinghua Ding,<sup>2</sup> Man He<sup>1</sup>

<sup>1</sup>School of Chemistry and Chemical Engineering, Southeast University, Jiangsu Optoelectronic Functional Materials and Engineering Laboratory, Nanjing 211189, China

<sup>2</sup>Kangdexin Photoelectric Material Co., Ltd, Zhangjiagang 215600, Jiangsu, China

Correspondence to: Y. Zhou (E-mail: ymzhou@seu.edu.cn)

**ABSTRACT:** In this article, a novel UV-curable epoxy acrylate oligomer (BPEFPGMA) with high refractive index is successfully prepared through semi-esterification reaction of 9,9-bis[4-(2-hydroxyethoxy)phenyl]fluorene and phthalic anhydride, followed by end-capping of glycidyl methacrylate. After 15 times' repetitions, the process and properties of this oligomer are stable and reliable. The resulting BPEFPGMA exhibited low solvent content ( $\leq 1600$  ppm), low viscosity (1900–2500 mPa s at 60°C), high refractive index ( $1.587 \pm 0.003$  at 20°C), and normal  $M_w$  (2550–3536 g/mol). The coating formulations of 1.57 UV-curable glue are mixed with BPEFPGMA as reactive oligomer. Through the technology of UV-curing forming, the corresponding brightness enhancement films are obtained. The resulting films exhibit normal structure, excellent adhesion (5B), good scratch resistance (50 g), and good abrasion resistance (50 g). They show excellent performance, and have reached the quality standard for use in liquid crystal display industry. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42386.

**KEYWORDS:** molding; monomers; oligomers and telechelics; resins

Received 26 January 2015; accepted 19 April 2015

DOI: 10.1002/app.42386

### INTRODUCTION

Liquid crystal display (LCD) is one of the most dynamic electronic products at the beginning of the 21st century. Its development broadens the application range of display, and made the electronic display more portable and popular. The development of LCD technology has gone through two generations.<sup>1–9</sup> In the first generation, considerable attention has been paid to the development of LCD with small size, light weight, and thin thickness. The growing social demand has led to a second generation of LCD with high brightness, high color reproduction, and wide viewing angle. Currently, the development stage of LCD is between the second and the third generation. Many studies have focused on the improvement of LCD with high brightness. It is well known that increasing the performance of brightness enhancement films (BEFs)<sup>10</sup> contributes to the improved brightness of LCD. Without altering the micro prismatic structure of the BEFs, the higher the refractive index itself, the greater its brightness. A series of oligomers as the active component of UV curable formulations have been prepared for higher refractive index. However, many of the applications of these oligomers are restricted due to the low refractive index, high viscosity, and the high price. Hence, there is considerable interest in preparing a series of novel oligomers both with high refractive index and best comprehensive properties.

Epoxy acrylate oligomer,<sup>11–14</sup> which has many advantages such as fast UV-curing speed, good chemical resistance, good adhesion, high hardness, low price, and so on, is now widely used in the field of UV curable. However, its refractive index is hard to be so high because of the limitations of structure. To circumvent this limitation, many researchers have attempted to introduce a structure with high refractive index into epoxy acrylate oligomers. In this regard, Kim *et al.*<sup>15</sup> synthesized an UV-curable difunctional sulfur-containing thioacrylate and thiourethane acrylate with high refractive index. However, the appearance of sulfur-containing oligomer is easy to turn yellow, and its application performances such as hardness and scratch are poor. Bisphenol A diglycidyl ether diacrylate (BDGDA),<sup>16</sup> in particular, has been used as the oligomer for high refractive index. However, with the development of LCD industry, its refractive index cannot meet the demand anymore. Hence, Kumar *et al.*<sup>17</sup> added SiO<sub>2</sub> nanoparticles as inorganic nano-reinforcing component to achieve higher refractive index. However, the inorganic/organic hybrid nanocomposite system introduces so many disadvantages that its comprehensive properties are very poor.

Fluorene<sup>18,19</sup> compound of the formula C<sub>13</sub>H<sub>10</sub> contains two benzene rings. 9,9-Bis[4-(2-hydroxyethoxy)phenyl]fluorene (BPEF) as a derivative of fluorene with four benzene rings was synthesized

by the condensation reaction of fluorenone and phenol under the catalysis of acid. In general, when the number of carbon atoms is the same, the refractive index of benzene ring is much greater than that of the saturated aliphatic ring. Moreover, the larger the benzene ring's share of the whole molecular weight, the greater its refractive index. Therefore, BPEF can be introduced into oligomers to improve its refractive index, which makes it has a simple synthesis process and good chemical stability. In addition, epoxy acrylate oligomer containing fluorene has the advantages of high heat resistance, high transparency, high refractive index, and low coefficient of linear expansion.

In the present work, a novel UV-curable epoxy acrylate oligomer (BPEFPGMA) with high refractive index is successfully prepared through semi-esterification reaction of BPEF and phthalic anhydride (PA), followed by end-capping of glycidyl methacrylate (GMA). After 15 times' repetitions, the process and properties of this oligomer are stable and reliable. The resulting BPEFPGMA exhibited low solvent content ( $\leq 1600$  ppm), low viscosity (1900–2500 mPa s at 60°C), high refractive index ( $1.587 \pm 0.003$  at 20°C), and normal  $M_w$  (2550–3536 g/mol). The coating formulations of 1.57 UV-curable glue are mixed with BPEFPGMA as reactive oligomer. Through the technology of UV-curing forming, the corresponding BEFs are obtained. The resulting films exhibit normal structure, excellent adhesion (5B), good scratch resistance (50 g), good abrasion resistance (50 g). They show excellent performance, and have reached the quality standard for use in LCD industry. This work not only provides a simple approach to synthesize an UV-curable epoxy acrylate oligomer with high refractive index by low cost, but also gives an excellent performance of forming BEFs with good basic properties in LCD industry.

## EXPERIMENTAL

### Materials

BPEF used in the experiment were purchased from Suqian Winstar Chemical Co., Ltd. Ortho-phenyl phenoxy ethyl acrylate (OPPEA) were purchased from Eternal Chemical Industry (China) Co., Ltd. PA, toluene, tetra butyl ammonium bromide (TBAB), 2,6-di-*tert*-butyl-4-methylphenol (BHT), and GMA which were analytically pure grade were purchased from Sino-pharm Chemical Reagent Co., Ltd.

### Characterization

The Fourier transfer infrared (FTIR) spectra analysis was performed on a Japanese SHIMADZU IRAffinity-1 type Fourier transform infrared spectroscopy in the  $1 \text{ cm}^{-1}$  resolution mode in the range of 800–4000  $\text{cm}^{-1}$  at room temperature. Ground powdery mixtures of sample and KBr were pressed into a tablet and then positioned in a vacuum oven at 80°C for 12 h. The liquid samples were filmed on the surface of ZnSe liquid tank.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were taken by a Bruker AVANCE 300 NMR spectrometer with tetra methylsilane (TMS) as internal reference, and deuterated chloroform ( $\text{CDCl}_3$ ) used as solvent. The weight distribution of the polymer was determined by an Agilent 1260 HPLC/GPC one machine with tetrahydrofuran as the solvent. Solvent content was measured by GCMS-QP2010 SE according to the internal standard method for toluene. Viscosity of samples was determined by HBDV-II+

Pro cone-plate viscometer, measured by a #52 rotor at a bath temperature of 60°C. Refractive index of samples was determined by ATAGO NAR-1T solid refractive index meter at a bath temperature of 20°C. The water content of samples was measured by Karl Fischer SF-5 moisture meter. Chroma was determined by using the Gardner Color as the color measurement standard. The closest Gardner scale numerals can designate the sample's chroma. Epoxy value of the sample is obtained by hydrochloric acid–acetone method.

*Acid value titration:* Acid value of the resins was determined by titration with 0.1 mol/L KOH according to the following procedure. The required amount of resin (0.5–1.0 g) was dissolved in acetone (20 mL) and titrated with 0.1 mol/L KOH using phenolphthalein as the indicator. End point of the titration was the first persistent faint pink color.

The formula is as follows:

$$A_v = \frac{c \times (V - V_0) \times 56.1}{m}$$

where:  $A_v$  = acid value of the sample (mgKOH/g);

$c$  = the concentration of KOH standard solution (mol/L);

$V$  = the volume of KOH standard solution consumed by the sample (mL);

$V_0$  = the volume of KOH standard solution consumed in the blank test (mL);

$m$  = the mass of the sample (g).

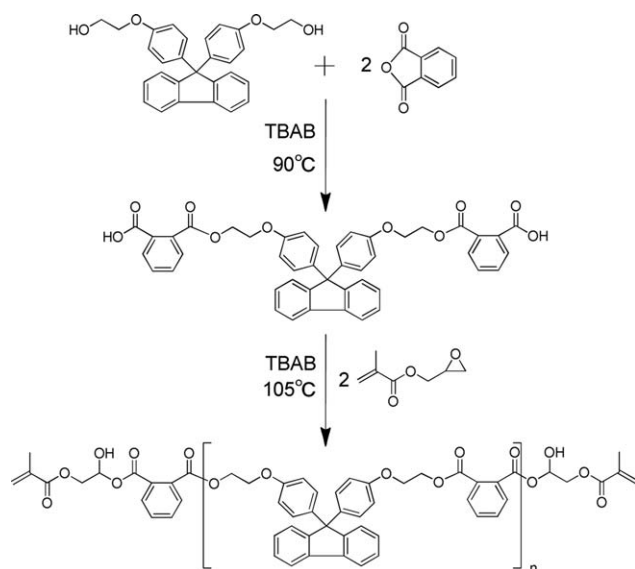
### Synthesis of BPEFPGMA

A certain amount of BPEF (123 g), toluene (200 g) as solvent were added into a four-necked round bottom flask (1000 mL) equipped with a mechanical stirrer, water separator, and thermometer. Then, the mixture was heated to 90°C until the BPEF dissolved in the toluene. Then followed by adding PA (83 g), TBAB (3 g), and BHT (0.2 g) in turn into the four-necked round bottom flask. The mixture was kept at 90°C for 2 h. After the acid value of the mixture reduced to 77 mgKOH/g, BHT (3 g) and TBAB (4 g) were added in turn into the four-necked round bottom flask. When the mixture was heated to 95°C, 80 g GMA (epoxy value = 0.6963 mol/100g) was added dropwise for 1 h. Then, the mixture was reacted at 105°C for 2 h until the acid value of the mixture is less than 5 mgKOH/g to prepare the epoxy acrylate oligomer containing fluorene (BPEFPGMA). Then, about 40% by wt of the OPPEA were dropped into the reactor to dilute the product. In order to get the crude product, the mixture was evaporated at reduced pressure and 60°C to remove the solvent.

## RESULTS AND DISCUSSION

### FTIR Analysis of BPEFPGMA

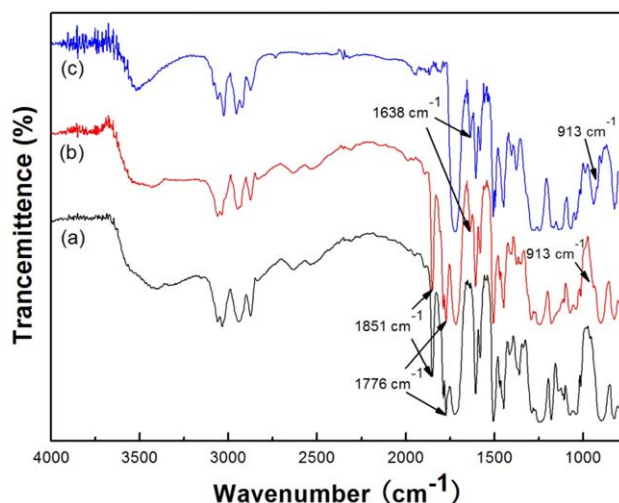
The overall reaction schemes for synthesis of BPEFPGMA are shown in Scheme 1. The fluorene-containing epoxy acrylate oligomer is synthesized by a two-step reaction. In the first step, the 1 : 2 mole ratio of BPEF and PA was used to synthesize the first-step product using TBAB as catalyst. The end point of the first-step reaction was characterized by acid value titration. In the second step, an excess of TABA as catalyst was used in order



**Scheme 1.** Synthesis of BPEFPGMA (the epoxy acrylate oligomer containing fluorene).

to get BPEFPGMA with a low acid value and to achieve a higher yield. The end point of the second-step reaction was characterized by FTIR and confirmed by the disappearance of the characteristic absorption peaks of acid anhydride group of PA and the appearance of the stretching vibration for the C=C group. Figure 1 shows the FTIR spectra of (a) the mixture of BPEF and PA; (b) the mixture of GMA and the first-step product; and (c) the final product.

In Figure 1(c), the appearance of an absorption peak at around  $913\text{ cm}^{-1}$  is attributed to the vibration of the epoxy ring. The disappearance of the peaks at  $1851\text{ cm}^{-1}$  and  $1776\text{ cm}^{-1}$  can be assigned to the characteristic absorption peaks of acid anhydride group. In Figure 1(c), the stretching vibration for the C=C group is around  $1638\text{ cm}^{-1}$ . Other characteristic peaks in the FTIR spectra all correlate well with the expected structure of BPEFPGMA.



**Figure 1.** FTIR spectra of BPEFPGMA: (a) the mixture of BPEF and PA; (b) the mixture of GMA and the first-step product; and (c) the final product. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

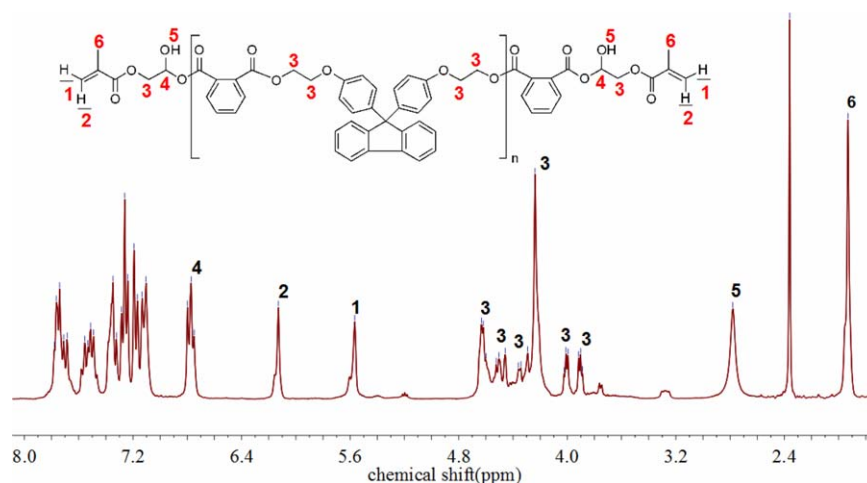
### <sup>1</sup>H-NMR Analysis of BPEFPGMA

Figure 2 shows the <sup>1</sup>H-NMR spectrum of BPEFPGMA in CDCl<sub>3</sub>.

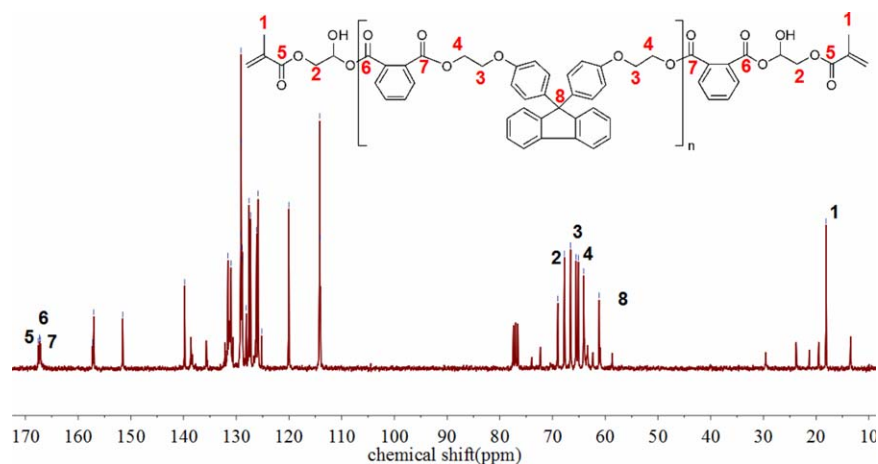
In Figure 2, the peak at 1.93 ppm is ascribed to the methyl groups (CH<sub>3</sub>) protons of BPEFPGMA and the peaks in the range of 3.89–4.63 ppm are the protons of methylene groups (CH<sub>2</sub>). The peaks in the range of 6.75–6.80 ppm are methine group (CH) protons of BPEFPGMA. Olefin protons are observed at 5.57–6.13 ppm which directly proves the appearance of acrylic double bond. Hydroxyl protons of BPEFPGMA are observed at 2.78 ppm. The peaks in the range of 7.10–7.78 ppm are the protons of benzene ring. Solvent residual peak is at 2.36 ppm.

### <sup>13</sup>C-NMR Analysis of BPEFPGMA

Figure 3 shows the <sup>13</sup>C-NMR spectrum of BPEFPGMA in CDCl<sub>3</sub>.



**Figure 2.** <sup>1</sup>H-NMR spectrum of BPEFPGMA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.**  $^{13}\text{C}$ -NMR spectrum of BPEFPGMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In Figure 3, the peak at 18.12 ppm is ascribed to the methyl group ( $\text{CH}_3$ ) carbon nuclei of BPEFPGMA and the peaks in the range of 64.10–68.99 ppm are the carbon nuclei of methylene groups ( $\text{CH}_2$ ). The peaks in the range of 167.32–167.57 ppm are methane groups ( $\text{CH}$ ) carbon nuclei of BPEFPGMA. Carbon nuclei (8) of BPEFPGMA are observed at 61.16 ppm. The peaks in the range of 114.08–157.26 ppm are the carbon nuclei of benzene ring and double bond. These data above fully reveal the preparation of BPEFPGMA.

#### Properties of BPEFPGMA

As shown in Figure 4, compared with the Gardner scale from No. 1 to No. 8, the chroma of BPEFPGMA is less than or equal to 3, and the appearance of the product is clear and transparent.

Moreover, after 15 times' repetitions, the process and properties of BPEFPGMA are stable and reliable. The resulting product exhibits low solvent content, low viscosity, high refractive index, and normal  $M_w$ . Figure 5 shows the fluctuation scatter diagrams of these properties above.

Performance indicators of BPEFPGMA are shown in Table I, which indicates that the properties of BPEFPGMA are stable and reliable.

#### FORMULATIONS AND FORMING OF BPEFPGMA

UV-curable technology,<sup>20</sup> which has many advantages of lower energy consumption, less environmental pollution, lower process costs, excellent film quality, rapid curing, low temperature operation, and high efficiency in production, is now widely used in the field of BEFs. UV-curable coating were basically formulated with a light curing initiator, monomers, oligomers, and some additives. Among them, oligomer is the key components to control the basic performance of corresponding BEFs.

BPEFPGMA as a novel epoxy acrylate oligomer containing fluorene has at least six benzene rings that occupy a large proportion of the whole molecular weight. In general, when the number of carbon atoms is the same, the refractive index of benzene ring is much higher than that of the saturated aliphatic ring. Moreover, the larger the benzene ring's share of the whole

molecular weight, the higher the refractive index. Therefore, after dilution by 40 wt % of the OPPEA, the refractive index of BPEFPGMA can still reach to 1.587, and its viscosity keeps very low. Therefore, BPEFPGMA can be widely used as reactive oligomer in the formulations of BEFs for higher refractive index.

BEFs have a specific structure of prismatic. In industrial production line, BEFs get its copy of micro-optical structure from a roller engraved with the pattern of prismatic through the technology of UV-curing forming. As to the laboratory research stage, the 0.4 Meter forming machine consistent with the actual production line has been used to obtain BEFs.

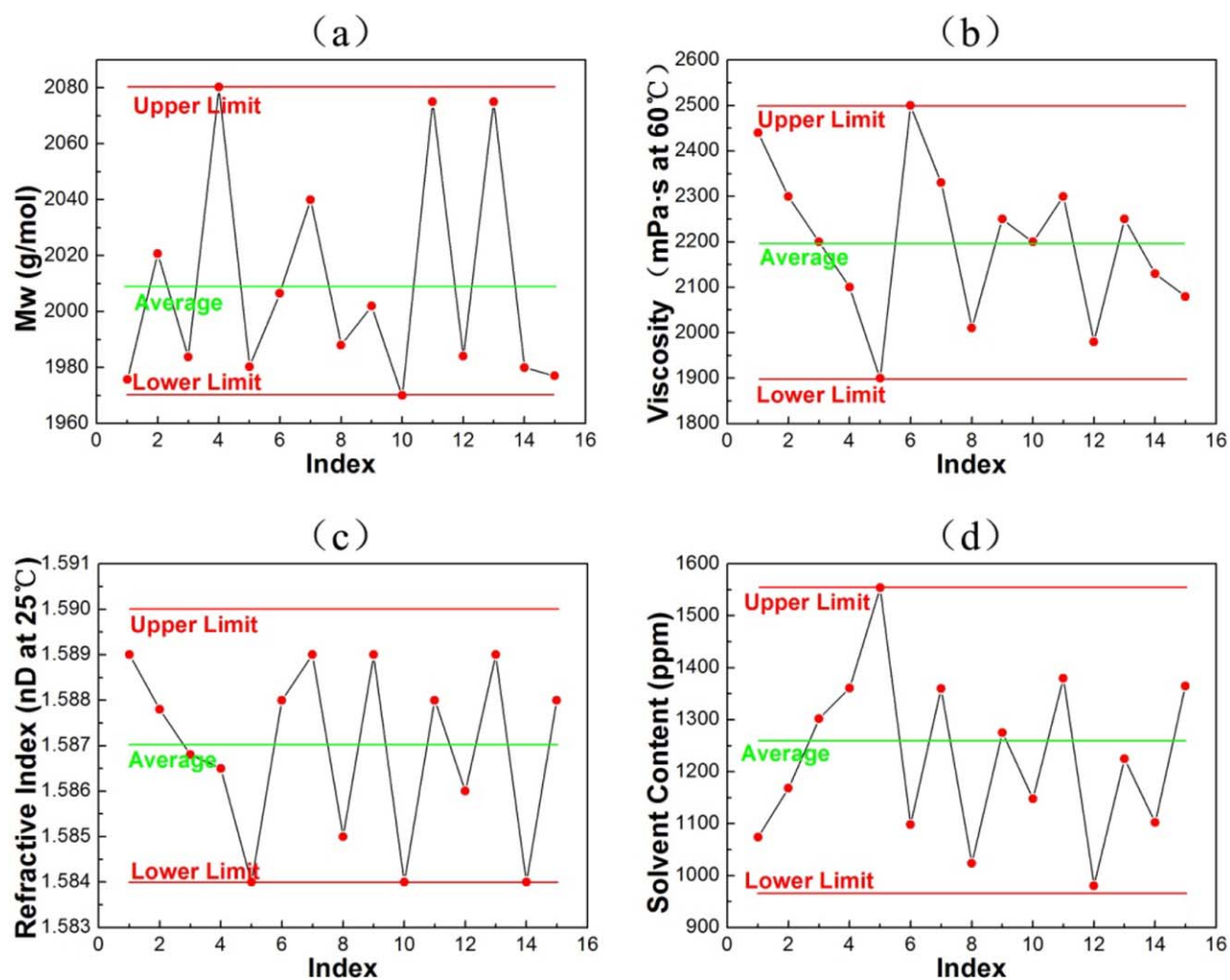
#### Formulation and Coating Preparation

Basic formulations of 1.57 refractive index UV-curing glue are shown in Table II.

BPEFPGMA is used as the high refractive oligomer in the formulation. The basic formulations of 1.57 UV-curing glue is mixed with solid photo initiator, BPEFPGMA, wear resistant oligomers, toughness oligomers, high refractive index monomers, and diluted monomers. The glue must be fully stirred at



**Figure 4.** The appearance of BPEFPGMA: (a) Gardner scale from No. 1 to No. 8; (b) BPEFPGMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 5.** Fluctuation scatter diagrams of BPEFPGMA: (a) weight average molecular weight ( $M_w$ ); (b) viscosity; (c) refractive index; and (d) solvent content. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

room temperature to make a complete homogeneous mixing. After all, the 1.57 refractive index UV-curing glue can be done.

### Forming

The film coating process of BEFs in 0.4 Meter forming machine is shown in Figure 6.

**Table I.** Performance Indicators of BPEFPGMA

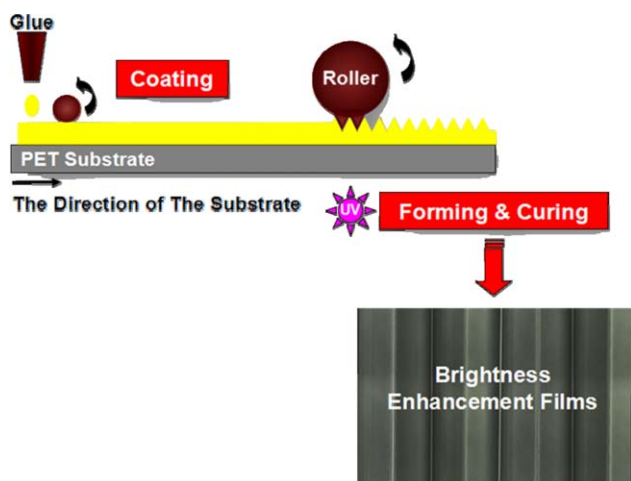
Properties	Unit	Indicators
Appearance	-	pale yellow liquid
Color	Gardner	$\leq 3$
Viscosity (60°C)	mPa s	1900-2500
Solvent content	ppm	$\leq 1600$
$M_w$	g/mol	1970-2080
Heat stability (90°C) <sup>a</sup>	hour	$\geq 2$
Refractive index (20°C)	-	$1.587 \pm 0.003$

<sup>a</sup>Heat stability test shows that after putting in the temperature of 90°C for at least 2 h, the oligomer did not polymerize.

The film coating process is divided into two steps: film coating and forming & curing. At first, as the PET substrate moves forward, the UV-curing glue covers the surface of the PET substrate uniformly with the help of the line bar. Then, under the UV light irradiation, the photo initiator in the wet films is activated and the radicals are produced. The formed radicals break the acrylate double bond of the monomers and oligomers that results in crosslinking, then, the roller with micro prism

**Table II.** Basic Formulations of 1.57 UV-Curing Glue

Basic formulations	Ratio (wt %)
BPEFPGMA	15-25
Wear resistant oligomers	20-30
Toughness oligomers	5-10
High refractive index monomers	25-35
Diluted monomers	15-25
Photo initiator	2-6



**Figure 6.** The schematic of the film coating process of BEFs in 0.4 Meter forming machine. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

structures copies its micro structure to the surface of the films. After demolding, the BEFs are obtained.

The micro structure of the BEFs after forming is shown in Figure 7.

#### Characterization of Films

The refractive index of UV-curing glue was measured by ATAGO NAR-1T solid refractive index meter at 25°C. The viscosity was measured by HBDV-II + Pro cone and plate viscometer with a #41 rotor at 25°C. The situation of film-forming was determined through whether there was abnormal sound during demolding. The adhesion of the films was assessed by using the "Lattice notch method". In brief, the cured films on glass sub-

**Table III.** Film-Forming Properties of BPEFPGMA

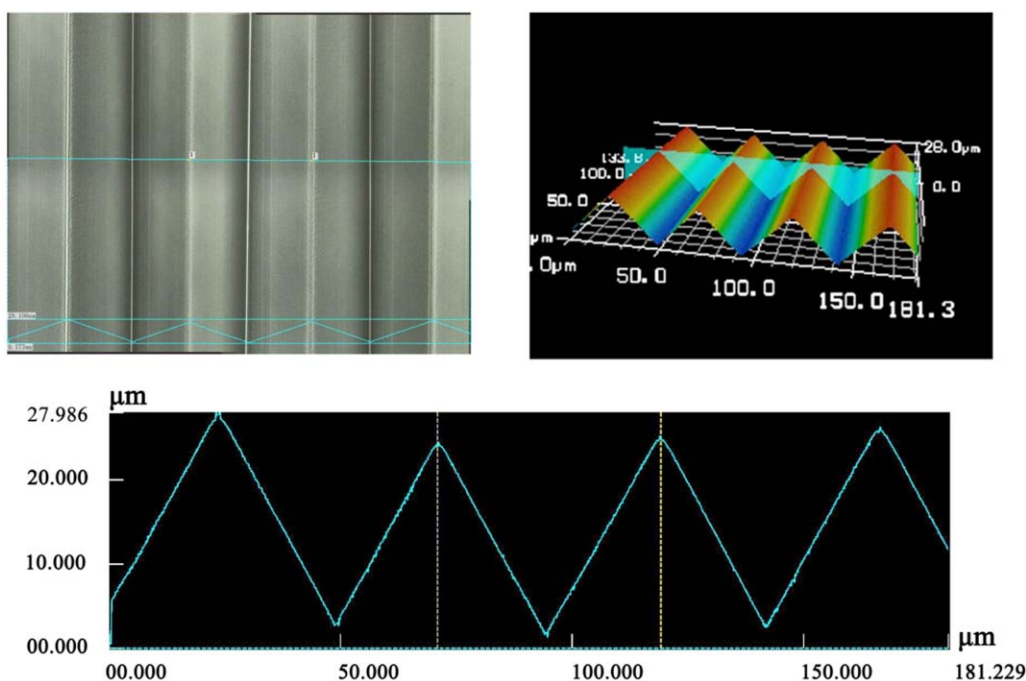
Properties	Indicators
Refractive index (nD at 25°C)	1.570
Thickness of the glue	24 $\mu\text{m}$
The situation of film-forming	good
Structure of BEFs <sup>a</sup>	normal
Adhesion	5B
Scratch performance	50 g
Wear resistant	50 g
Luminance	5191

<sup>a</sup>The situation of forming process: structure B, 4 kg pressure, 4m/min, a mold temperature of 45°C, and the plastic temperature is at room temperature.

strates are divided into small squares by razor blade. Then, the insulating tape is used to place over the surface of the films and pulled from the films. If there are no squares that detached from the glass substrates, its adhesion can be presented by "5B" as the highest level, which indicates that the cut edge is completely smooth and lattice edges without any flaking. "4B"-"0B" level so. Wear resistance of the films was measured by 339 abrasion testing machine. Scratch performance was achieved by PV 3952 scratch resistance tester. Luminance was measured by Topcon BM-7 luminance tester.

#### Film-Forming Properties

Film-forming properties of BPEFPGMA are shown in Table III. Through the technology of UV-curing forming, the corresponding BEFs can be obtained. The resulting films exhibit normal structure, excellent adhesion, good scratch resistance, and good



**Figure 7.** The micro structure of the BEFs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

wear resistant. They all show excellent performance, and have reached the quality standard for use in LCD industry.

## CONCLUSIONS

In this article, a novel UV-curable epoxy acrylate oligomer containing fluorene with high refractive index is successfully prepared through semi-esterification reaction of BPEF and PA, followed by end-capping of GMA. After 15 times' repetitions, the process and properties of this oligomer are stable and reliable. The resulting BPEFPGMA exhibits low solvent content ( $\leq 1600$  ppm), low viscosity (1900–2500 mPa s at 60°C), high refractive index ( $1.587 \pm 0.003$  at 20°C), and normal  $M_w$  (2550–3536 g/mol). The coating formulation of 1.57 UV-curable glue is mixed with BPEFPGMA as reactive oligomer. Through the technology of UV-curing forming, the corresponding BEFs are obtained. The resulting films exhibit normal structure, excellent adhesion (5B), good scratch resistance (50 g), good abrasion resistance (50 g). They all show excellent performance, and have reached the quality standard for use in LCD industry. This work not only provides a simple approach to synthesize an UV-curable epoxy acrylate oligomer with high refractive index by low cost, but also gives an excellent performance of forming BEFs with good basic properties in LCD industry.

## ACKNOWLEDGMENTS

The authors are grateful for the financial support from Kangdexin Photoelectric Material Co., Ltd. (Jiangsu), Jiangsu Photoelectric Functional Materials Engineering Laboratory, the Fundamental Research Funds for the Central Universities (No. 3207045301), Fund Project for Transformation of Scientific and Technological Achievements of Jiangsu Province of China (No. BA2011086).

## REFERENCES

- Mingyan, L.; Daming, W.; Yajun, Z.; Jian, Z. *Procedia Eng.* **2011**, *16*, 306.
- Li, C. J.; Fang, Y. C.; Cheng, M. C. *Optik* **2010**, *121*, 2245.
- Kuo, H. P.; Chuang, M. Y.; Lin, C. C. *Powder Technol.* **2009**, *192*, 116.
- Joo, B. Y.; Shin, D. H. *Displays* **2010**, *31*, 87.
- Joo, B. Y.; Shin, D. H. *Displays* **2009**, *30*, 190.
- Chu, C. Y.; Pan, M. C. *Adv. Eng. Softw.* **2010**, *41*, 130.
- Chiu, T. L.; Lee, J. H. *Opt. Commun.* **2010**, *283*, 373.
- Chen, C. F.; Wu, C. C.; Wu, J. H. *Optik* **2010**, *121*, 847.
- Cai, C.; Nunes, R.; Lien, A.; Galligan, E.; Levon, K. *J. Appl. Polym. Sci.* **1999**, *73*, 1197.
- Sun, Z.; Chang, J.; Zhao, N.; Jin, W.; Wang, Y. *Optik* **2010**, *121*, 760.
- Cui, J.; Yu, G.; Pan, C. *J. Appl. Polym. Sci.* **2014**, *131*, 41067.
- Xu, D. M.; Zhang, K. D.; Zhu, X. L. *J. Appl. Polym. Sci.* **2004**, *92*, 1018.
- Matynia, T.; Kutyłkeja, R.; Bukat, K.; Pieńkowska, B. *J. Appl. Polym. Sci.* **1995**, *55*, 1583.
- Saxena, A.; Francis, B.; Rao, V. L.; Ninan, K. N. *J. Appl. Polym. Sci.* **2007**, *106*, 1318.
- Kim, J. S.; Cho, B. S.; Kweon, J. O.; Noh, S. T. *Prog. Org. Coat.* **2014**, *77*, 1695.
- Kumar, V.; Bhardwaj, Y. K.; Goel, N. K.; Francis, S.; Dubey, K. A.; Chaudhari, C. V.; Sarma, K. S. S.; Sabharwal, S. *Surf. Coat. Technol.* **2008**, *202*, 5202.
- Kumar, V.; Misra, N.; Paul, J.; Bhardwaj, Y. K.; Goel, N. K.; Francis, S.; Sarma, K. S. S.; Varshney, L. *Prog. Org. Coat.* **2013**, *76*, 1119.
- Lázár, L.; Nagy, M.; Rácz, D.; Zsuga, M.; Kéki, S. *Tetrahedron* **2014**, *70*, 3691.
- Jiang, H. J.; Feng, J. C.; Wang, H. Y.; Wei, W.; Huang, W. *J. Fluorine Chem.* **2006**, *127*, 973.
- Wu, J.; Ma, G.; Li, P.; Ling, L.; Wang, B. *J. Appl. Polym. Sci.* **2014**, *131*, 40740.