Radiation-Curable Oligomers with High Refractive Index

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Abstract

The present work addresses a strong market demand for antireflection (AR) coatings. AR coatings consist of at least one thin film with a high refractive index (n_D). We prepared organic radiation (UV)-curable oligomers with $n_D > 1.6$. We found a novel way of preparation of sulfur containing UV-curable high n_D oligomers, based on melamine and urethane acrylates. n_D of synthesized liquid oligomers was 1.56 ÷1.62. UV-cure of oligomers led to 1-5% increase in n_D. Coatings based on these oligomers are easy to cure; they demonstrate good adhesion to different substrates and possess excellent mar-resistance and anti-fog properties.

Keywords: UV-cure; oligomers; antireflective coating; refractive index; melamine acrylates; urethane acrylates; flat panel display; optical coating

Introduction

Anti-reflection (AR) coatings or films allow reduction of reflective losses at the substrate/air interface. AR coatings reduce reflection, increase light transmittance, and they are very important in all types of displays, portable terminals, and in optical industry (solar cells, light fixtures, optical lenses, etc.). A typical AR coating consists of successive alternating thin layers of high and low refractive index (n_D) films, cf. Figure 1:

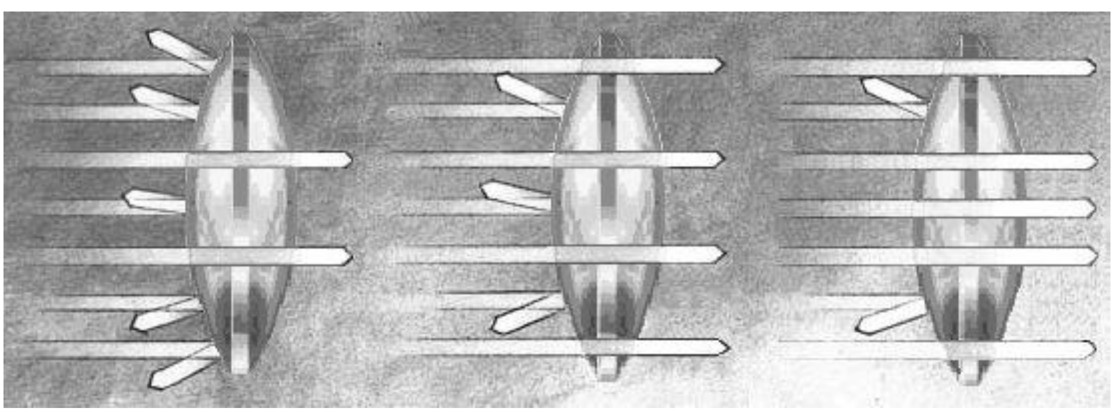

Figure 1. Schematic presentation of action of AR coating (Luxorion web site). From left to right: a lens without coating; single layer of AR coating; multiple layers. Transmittance increases up till 99.5%.

In the ideal situation, 100% of normal incident light will be transmitted if a single layer of AR coatings with its n_D^{AR} and thickness l satisfies the following two simple equations:

$$n_D^{AR} = (n_D^{S})^{1/2}, \qquad (1)$$

n_D of air is equal 1.0; n_D^S is n_D of a substrate,

$$n_D^{AR} * l = \lambda_D/4 , \qquad (2)$$

Eq. 1 follows from Frensel equation, and eq. 2 represents a demand of a destructive interference of the incident and reflected from the bottom of AR film light. That way no reflection takes place. (Refractive index depends upon temperature and λ. Usually n are presented as n_D, where λ_D = 589 nm, the sodium D-line.)

A commonly used substrate in optical applications is polycarbonate with n_D = 1.58-1.59 (Brandrup *et al* 1999*)*. Thus, coating with n_D > 1.59 is desirable. In the present work we deal with only with the synthesis and properties of high n_D oligomers. We synthesized UV-curable thioether and thiourethane monomers and oligomers for high n_D coatings. In a number of experiments we used as a starting compound melamine acrylates, which have a relatively high content of aromatic groups and nitrogen atoms. The melamine acrylate used has a high n_D of 1.512.

Anti-reflection coatings see significant recent use in the manufacture of flat panel displays and other optically sensitive assemblies. High refractive index oligomers may have additional value in the fiber optic coatings market.

EXPERIMENTAL

Reagents

Thiophenol, triphenylmethanethiol, p-thiocresol, 2-mercaptothiazoline, and 2-mercaptobenzothiazole, 2-hydroxyethyl acrylate (HEA) were purchased from Aldrich. Melamine acrylates BMA-222 and XMA-224 are Bomar™ oligomers. BMA-222 is trifunctional and XMA-224 is a pentafunctional acrylate, cf. Figure 2:

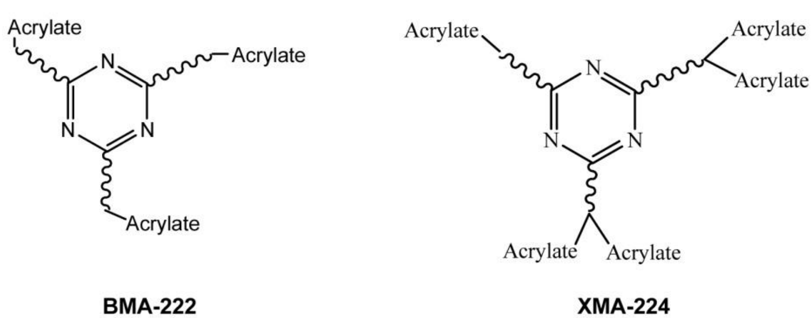

Figure 2. Generic structure of the used melamine acrylates

Diisocyanates 4,4’-methylenebis(phenyl isocyanate) (MDI) and tolylene diisocyanate (TDI 80/20) were of Rhodia. Photoinitiator (PI) Omnirad-73 of IGM Resins was added in the level of 1% to the studied formulations. Polysulfide $(C_2H_4OCH_2OC_2H_4SS)_mC_2H_4OCH_2OC_2H_4$ was of Toray Company (Japan). Common reactive diluents IBOA and TRPGDA were of Sartomer.

Devices

All the products in discussed in this study were analyzed with gel permeation chromatography (GPC) and infrared spectrometer (IR). GPC device of Polymer Labs PL-GPC 50 was equipped with an RI detector and mixed D columns. The IR spectrometer was Perkin-Elmer Spectrum One model with a diamond crystal UATR. Formulations were cured in the air with a Fusion 300 processor; D-bulb, belt speed 20 ft/min, one pass. n_D of liquid oligomers was measured with Abbé refractometer. n_D of cured films were measured with a technique using different refractive index oils. In this method a sample of a cured film and known refractive index oil were squeezed in between glass microscope slides. When the refractive indices of the film and the oil were different, the boundaries of the film were visible through a Nikon transmission optical microscope. The Becke Line Method was utilized to narrow down the matching refractive index oil. The test was repeated until the refractive indices of the oil and the film matched.

Results

We used two routes to include sulfur-containing compound into our UV-curable oligomers. The first route was the well-documented Michael addition reaction of RS-H to electron deficient enones such as maleimides (Houseman *et al* 2003) and acrylates (Ludolf *et al* 2001) The second route utilizes formation of thiourethanes upon addition of thiols to isocyanates ().

Addition of thiols to melamine acrylates

In the first route we selected BMA-222 and XMA-224, cf. the Reagents section above. Both melamine acrylates have low viscosities (η = 2000 cP at room temperature) and can be cured at relatively low exposure (high belt speed) and at very low PI concentration. Reactions of these melamine acrylates with various aromatic thiols listed in the Reagents section above, led to new family of melamine acrylates. The products of reaction of melamine acrylates with thiols have higher n_D than that of original melamines. Namely, refractive indices of the melamine acrylates, XMS-222, XMS-2240, XMS-2241, XMS-2242, and XMS-2243, were 1.552, 1.566, 1.589, 1.593 and 1.600, respectively. All the melamine acrylates gave transparent films after UV-cure. We noticed that n_D of a cured oligomer increased by 1-5 % compared to n_D of a liquid oligomer in our experiments. XMS-2240 was particularly interesting because of its relatively low cost, color, and viscosity (~5000 cP at room temperature). Composition of three formulations based on XMS-2240 and some mechanical properties of cured formulations are presented in the Table 1.

Table 1. Formulations and mechanical properties of XMS-2240 based films F-1to F-3[a]

	F-1	F-2	F-3
XMS-2240 (wt.%)	99	69	49
IBOA (wt.%)	-	30	-
TRPGDA (wt.%)	-	-	50
Omnirad-73 (wt.%)	1	1	1
Viscosity[b] (cP)	5400	400	150
Tensile Strength[b] (MPa)	87	270	399
Elongation-at-break[b] (%)	8	30	5
Tensile Modulus[b] (MPa)	1.2	2.9	51
Durometer Hardness[b]	74	73	54

[a] Data at room temperature. [b] Determination error is 10%

Thiourethane acrylates

A number of thiourethane acrylates were also prepared by the reaction of thiols or polysulfide with aromatic isocyanates with a subsequent capping of the residual isocyanate groups with HEA. In general, polythiourethanes high tensile strengths and excellent abrasion resistance (Saunders and Frisch 1964, Okubo *et al* 1998). Moreover, polysulfide based thiourethanes show good oil resistance properties (Quan *et al* 2004). The typical chemical structures of the synthesized products are presented in Figure 4.Refractive index values of the obtained oligomers were between 1.575 and 1.615. n_D increased by 1-4 % when the thiourethane acrylate oligomers were UV-cured. The highest refractive index of our films was 1.66. Among these oligomers polysulfide based thiourethane acrylate was particularly interesting because of the flexibility and low cost, cf. Table 2.

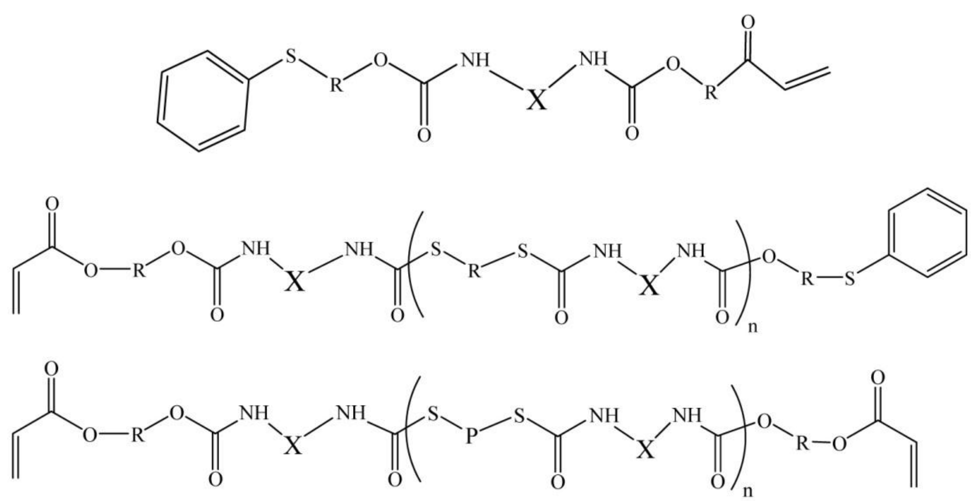

Figure 4: Representation of the structures of thiourethane acrylates. Here X stands for aromatic group; R stands for alkyl, and P stands for polysulfide, cf. Reagents section above.

Table 2. Formulations and mechanical properties of polysulfide-thiourethane acrylate based films F-4 and F-5[a]

	F-4	F-5
Polysulfide-thiourethane acrylate (wt.%)	69	49
IBOA (wt.%)	30	-
TRPGDA (wt.%)	-	50
Omnirad-73 (wt.%)	1	1
Viscosity[b] (cP)	49000	3950
Tensile Strength[b] (MPa)	1370	1920
Elongation-at-break[b] (%)	97	18
Tensile Modulus[b] (MPa)	18	78
Durometer Hardness[b]	74	91

[a] Data at room temperature. [b] Determination error 10%

Discussion

High refractive index materials often obtained with inorganic/organic hybrid systems. However, to produce a transparent coating, metal oxide particles should be formed *in situ* at high temperatures (>300°C). To the best of our knowledge, the highest reported refractive index organic polymer is n_D of 1.757 (Sadayori and Hotta 2004). At the same time, the polymer was cast from an aprotic solvent.

There is a commercial interest in coatings with high refractive index, which can be obtained at mild conditions, at ambient temperatures, and with low or zero VOC. Therefore, UV-cured, high n_D coatings attract much attention from both academia and industry (Molford *et al* 2006, Flaim *et al* 2004, Williams 1999). Besides all the known advantages of UV-curable formulations, UV-cure leads to increased n_D under cure due to an increase in molecular polarizability through molecular orientation and volume shrinkage.

Polymers containing aromatic groups and highly polarizable atoms such as sulfur, phosphorus, bromine, and iodine show relatively high refractive index values (Groh and Zimmermann 1991, Olshavsky and Allcock 1997). Among those, sulfur containing polymers are of special interest due to their low color, raw material availability and variety of mechanical properties. Formation of thioethers and thiourethanes through addition reactions to enes and isocyanates, respectively, has been known for a long time (Bell 1950, Zhu *et al* 1997).

In this study, we have focused on the synthesis of UV-curable thioether and thiourethane monomers and oligomers with a goal of producing high n_D coatings. Nucleophile character of thiols RS-H allows synthesis of C-S bond containing products with a high yield.

Melamine acrylates are well known resins in coatings industry. Earlier we have introduced a new class of UV-curable melamine acrylate resin (BMA-222) as depicted in Figure 2 (DeSousa and Khudyakov 2006). This trifunctional acrylate resin BMA-222 was produced by the reaction of a melamine resin and HEA. Furthermore, we have produced a five-acrylate functional melamine acrylate (XMA-224) to obtain lower viscosities and harder materials, cf. Figure 2. Both melamine acrylates have relatively high n_D = 1.512 due to relatively high concentration of aromatic groups and nitrogen atoms. In this study we were able to increase the n_D of the studied melamine acrylate oligomers up to 1.6 with a thiol modification. The films obtained from XMS-2240 have low tensile strength due to a low concentration of acrylate groups and probably low crosslink density. Addition of more thiols to acrylates consumes acrylate groups available for UV cure, and hence decreases the tensile strength and toughness of the cured coatings. Therefore, there is a tradeoff between mechanical properties and refractive index in the approach with thiol addition.

Thiourethane acrylates demonstrate excellent mechanical properties compared to such properties in thiol-modified melamine acrylates. As expected, they have much higher viscosities. The most important problem for thiourethanes is the availability of low cost and low color thiol oligomers. Unfortunately, low cost polysulfides have reddish yellow color.

All of the oligomers synthesized in this study had excellent cure efficiency. Thiol modified melamine acrylates could be easily cured, even with 0.2% of PI.

Conclusion

New UV-curable oligomers with high refractive index were synthesized for an application in antireflection coatings. Oligomers exploit presence of sulfur atoms and aromatic rings as constituents, leading to an increase of n_D. At the same time, cured oligomers (coatings) possess valuable properties as protective coatings for plastics.

References

Bell, R.T. 1950. Synthesis of thioethers, *US Patent 2535831*

Brandrup J., Immergut E.H. and Grulke E.A., 1999. *Polymer Handbook*, Wiley, New York, VI, p.571.

DeSousa, J.D. and Khudyakov, I.V. 2006. Ultraviolet (UV)-curable amide imide oligomers, *Industrial & Engineering Chemistry Research.* 45 : p.19

Flaim, T.D., Wang, Y., and Mercado, R. 2004. High refractive index polymer coatings for optoelectronics applications, *Proceedings of SPIE-The International Society for Optical Engineering*. p. 5250

Groh, W. and Zimmermann, A. 1991. What is the lowest refractive index of an organic polymer? *Macromolecules*. 24 : p. 6660

Houseman B.T., Gawalt E.S. and Mrksich M. 2003. Maleimide-functionalized self-assembled monolayers for the preparation of peptide and carbohydrate biochips, *Langmuir*. 19 : p. 1522
http://www.astrosurf.com/luxorion/reports-coating.htm

Ludolf N.P., Tirelli N., Cerritalli S., Cavlli L. and Hubbell J.A. 2001. Systematic modulation of Michael-type reactivity of thiols through the use of charged amino acids, *Bioconjugate Chemistry*. 12 : p. 6536

Molford, R., Shih, W. and Dachsteiner, J. 2006. *Proceedings of SPIE-The International Society for Optical Engineering.* p. 6123

Okubo, T. Kohmoto, and S. Yamamoto, M. 1998. Synthesis, characterization, and optical properties of polymers comprising 1,4-dithiane-2,5-bis(thiomethyl) group, *Journal of Applied Polymer Science.* 68: p. 1791

Olshavsky, M. and Allcock, H. R. 1997. Polyphosphazenes with high refractive indices: optical dispersion and molar refractivity, *Macromolecules*. 30 : p. 4179

Quan, Y.W., Dong, W.Z., Fang, J.L., and Chen, Q.M. 2004. Ultraviolet curing of liquid polysulfide thiourethane acrylate, *Journal of Applied Polymer Science*. 91: p. 2358

Sadayori, N and Hotta, Y. 2004. Polycarbodiimide having high index of refraction and production method thereof, *US Patent Application Publication 20040158021A1*

Saunders, J.H. and Frisch, K.C., 1964. *Polyurethane chemistry and technology*, Wiley, New York

Williams, T.R. 1999. Scratch resistant optical films and method for producing same, *US Patent* 5900287

Zhu, Z., Risch, B.G., Yang, Z. and Lin, Y.N. 1997. Optical thermoplastic thiourethane-urethane copolymers, *US Patent* 5679756