

New UV-Curable High Refractive Index Oligomers

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The present work addresses a market demand for high refractive index (n_D) coatings. We prepared organic UV-curable oligomers with $n_D > 1.6$. We found a novel way to prepare sulfur-containing UV-curable high n_D oligomers of melamine and urethane acrylates. Refractive indices of the synthesized oligomers were between 1.552 and 1.615. Cure of the oligomers led to films with $n_D=1.559$ and 1.660. A wide variety of mechanical properties for UV-cured oligomers can be obtained with the facile synthesis methods used.

Introduction

Antireflective (AR) coatings allow reduction of reflective losses at the substrate/air interface. AR coatings reduce reflection, increase light transmittance and are therefore important for displays, portable terminals and the optical industry (solar cells, light fixtures, optical and ophthalmic lenses, etc.). A typical AR coating consists of successive alternating thin layers of high and low refractive index (n_D) films. A commonly used substrate in optical lenses is polycarbonate with $n_D = 1.58-1.59$.¹ Thus, a multilayer AR coating should have at least one layer with $n_D > 1.59$.

The known high n_D polymers mostly consist of conjugated systems containing heavy atoms such as bromine and iodine.^{2,3} However, most of these polymers exhibit undesirable intense colors.⁴ Polyphosphazenes and sulfur containing polymers were extensively studied as colorless materials with high n_D .^{2,5,6,7}

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Organic/inorganic hybrid systems have been widely studied as materials with very high refractive indices. However, phase separation, brittleness, cracking, and high optical dispersion are known problems in the application of organic/inorganic hybrids.^{8,9} Furthermore, production of these materials often requires high temperatures, usually more than 300 °C. To the best of our knowledge, the highest reported n_D of an organic polymer is 1.757.¹⁰ However, the polymer was prepared not by UV-cure but was cast from a solvent.¹⁰

Radiation-curable and in particular UV-curable high n_D oligomers have advantages over the high n_D oligomers described above. UV-cured high n_D coatings have been studied in both academia and industry.^{11,12,13} UV-cure has the known advantages of a short cure time, ambient temperature cure, lack of solvent emission, efficiency and low energy consumption. Furthermore, photopolymerization leads to an increase of n_D of the coating due to increase in molecular polarizability through molecular orientation and volume shrinkage.

In the present work, we have studied sulfur containing UV-curable high n_D oligomers. Thioether and thiourethane acrylate oligomers were synthesized. Melamine acrylates, which have relatively high content of (hetero)aromatic groups and nitrogen atoms, were used in syntheses of high n_D thioether compounds.

Experimental Section

Reagents. Thiophenol, *p*-thiocresol, triphenylmethanethiol, 2-mercaptothiazoline, 2-mercaptobenzothiazole, *N*-methylaniline, 2-aminobenzothiazole, and 2-hydroxyethyl acrylate (HEA) were from Aldrich. Melamine acrylates, BMA-222 and BMA-224 are the

products of Bomar Specialties.¹⁴ BMA-222 is mainly trifunctional and BMA-224 is mainly pentafunctional acrylate, cf. Figure 1:¹⁴

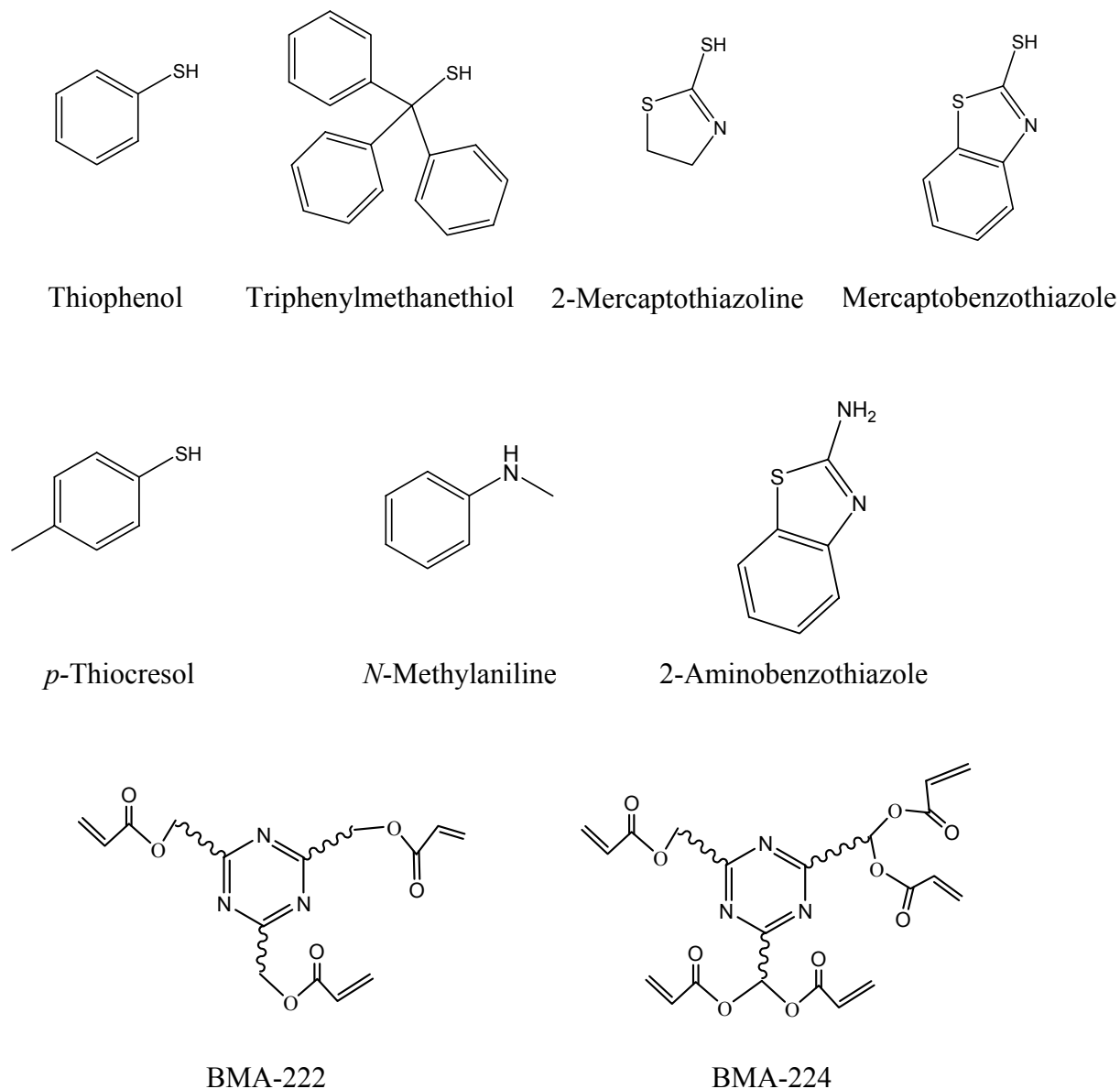


Figure 1. Chemical structures of thiols, amines and generic structures of the melamine acrylates.

Diisocyanates 4,4'-methylenebis(phenyl isocyanate) (MDI) and tolylene diisocyanate (TDI 80/20) were of Rhodia. Photoinitiator (PI) Omnirad-73 of IGM Resins,

which is 2-hydroxy-2methyl-1-phenylpropan-1-one, was added in the level of 1.0% to all the studied formulations. Polysulfide $(C_2H_4OCH_2OC_2H_4SS)_mC_2H_4OCH_2OC_2H_4$ was of Toray (Japan). Reactive diluents isobornyl acrylate (IBOA) and tripropyleneglycol diacrylate (TRPGDA) were products of Sartomer. All chemicals were used as received.

Instruments. All the products 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 FT-IR spectrometer was Perkin-Elmer Spectrum One model with a diamond crystal UATR. Formulations were cured in air with a Fusion 300 processor, D-bulb, belt speed 20 ft/min, one pass. n_D of liquid oligomers were measured with Abbé refractometer. n_D of cured films were measured with oils of different n_D . In this method a sample of a cured film and a small amount of oil with a known n_D 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 used to narrow down the matching refractive index oil. The test was repeated until the refractive indices of the oil and the film matched.

The viscosity was measured with a Brookfield RVT viscometer with a small adapter (spindle SC4-15 and cup 7R). The tensile properties of cured samples (elongation-at-break, tensile strength at break, tensile modulus) were measured with a ChemInstruments Tensile Tester-1000 system. The test method was designed to be in compliance with ASTM Standard D 882. The tester was controlled by the Cheminstruments EZ-Lab system software. At least five samples of each cured formulation were studied at ambient temperature, to verify reproducibility of the data.

The hardness of the cured films was measured with a Type D durometer (Shore D, model 307L, PTC Instruments).

All measurements in this in this work were performed at room temperature and all numerical values presented in this paper were measured at the room temperature.

Results and Discussion

In this study, two different routes were used to prepare sulfur-containing UV-curable oligomers. The first route utilized the well-documented Michael addition of thiols (RS-H) to electron deficient acrylates.¹⁵ The second route was through formation of thiourethanes upon reaction of thiols with isocyanates.¹⁶ Formation of thioethers and thiourethanes by addition reactions to enes and to isocyanates, respectively is well-documented.^{17,18}

Addition of thiols to melamine acrylates. Melamine acrylates can be good starting materials for synthesis of high n_D oligomers because they already have relatively high un-modified n_D of 1.512. The high n_D of melamine acrylates is due to the presence of nitrogen atoms in melamine molecules.¹⁹ Structures of UV-curable melamine acrylate resins BMA-222 and BMA-224 are presented in Figure 1.¹⁹ BMA-222 and BMA-224 have acrylate functionalities three and five, respectively. These two melamine acrylates have relatively low viscosities for oligomers ($\eta \sim 2000$ cP). Oligomers can be cured at relatively short times (high belt speed) and at low PI concentrations (less than 1.0%).¹⁹ It is desirable to preserve such properties (fast cure response and low viscosity) in high n_D oligomers.

Reactions of BMAs with aromatic thiols led to a new family of melamine acrylates. Throughout this paper such adducts will be abbreviated as X_i , cf. Table 1. GPC

traces and IR spectra of BMA-224 and \mathbf{X}_1 (cf. Table 1 for \mathbf{X}_1) are presented in Figure 2 and 3, respectively. Weight average molecular weight (\overline{M}_w) and polydispersity (P_d) of the BMA-224 and \mathbf{X}_1 are given in Table 1.

Table 1. Molecular weight and n_D of BMA-224 and its thiol adduct \mathbf{X}_1

Oligomer	\overline{M}_w	P_d	BMA^a	Thiol	n_D^b (oligomer)	$n_D^{b,c}$ (film)
BMA-224	1100	1.23	–	–	1.512	1.521
\mathbf{X}_1	1200	1.34	BMA-224	Thiophenol	1.566	1.578

^bDetermination error of n_D is ± 0.002

^cCured with 1.0% PI. Thickness of the films were $\sim 100 \mu\text{m}$.

As depicted in Figure 2, all the peaks shifted slightly to lower retention times (higher MW) due to thiophenol addition to the acrylate groups, which evidently leads to an increase of MW. The area under the peak number 3 was significantly increased in the product (\mathbf{X}_1), cf. Figure 2. Peak 3 reflects a contribution of low MW fraction into BMA-222 with many acrylate groups. A relative increase of MW of a fraction reflected by the peak 3 should be especially noticed compare to other peaks. Higher molecular weight oligomers are mainly the result of the self condensation of the alkoxy groups of melamines.²⁰ Therefore, higher molecular weight melamine acrylate oligomers contain more melamine linkages and less acrylate groups per mass unit. A relative increase in MW of high MW fractions of BMA-222 upon addition of thiol is smaller, cf. Figure 2, variation of peaks (a shoulder) 1,2.

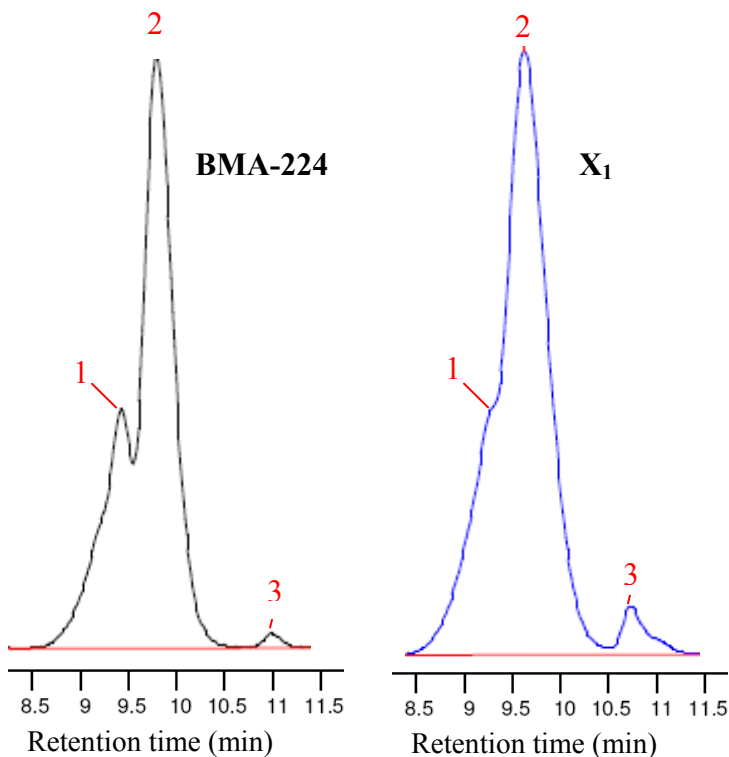


Figure 2. Gel permeation chromatograms of BMA-224 and X_1 . Peaks and a shoulder on GPC traces are marked as 1-3.

The reaction of the thiols with acrylate double bonds was monitored by disappearance of the peak intensity of absorption band around 810 cm^{-1} . Carbonyl peak at 1720 cm^{-1} was used as an internal standard. All the reactions were continued until the expected acrylate peak intensity decreases to a certain constant value. Evidently, at this point all thiols have reacted with acrylates. There is an expected agreement between the stoichiometry of the reaction and the observed decrease of acrylate absorption in IR spectra. One can see from the Figure 3 that acrylate peak intensity of X_1 is $\sim 40\%$ of the intensity of the same peak in BMA-224. *In this work all adducts X_i were prepared such that 60% of the acrylate groups of the starting BMA were consumed in addition reaction,* cf. Table 2.

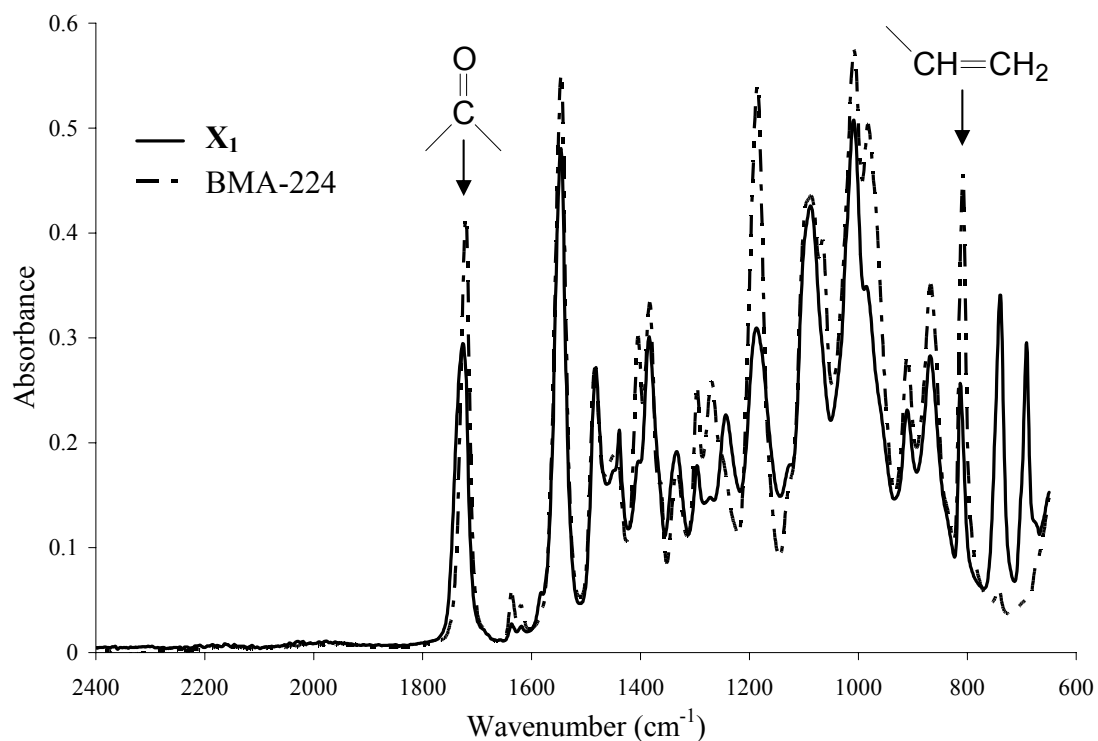


Figure 3. IR spectra of BMA-224 and X_1 .

The products of the reaction of melamine acrylates with thiols have higher n_D than that of the original melamines. In order to understand how thiol addition affects n_D , BMA-224 was modified with different amounts of thiophenol, cf. Figure 4, An increase of thiol to initial acrylate ratio leads to a gradual increase of n_D of the adduct, see Figure 4.

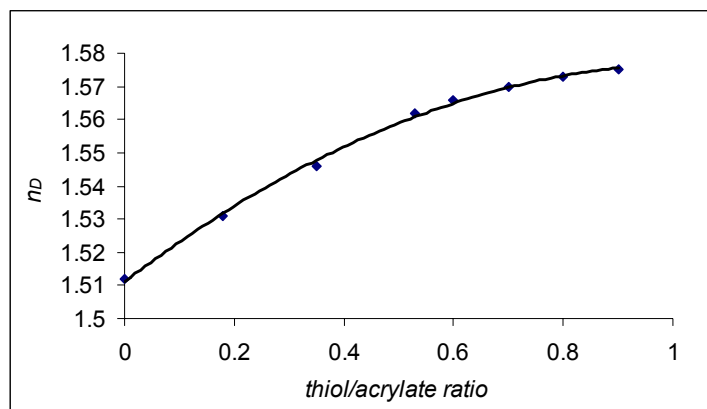


Figure 4. Dependence of n_D of adducts of BMA-224 to thiophenol upon initial thiol/acrylate molar ratio.

Molecular weight information and refractive indices of different melamine acrylates obtained via modification with various thiols at a molar ratio of 0.6 of thiol to initial acrylate were listed in Table 2. The structures of thiols essentially affect n_D of adducts, X_i , cf. Table 2. We were able to get n_D of modified melamine acrylate oligomers up to 1.6, cf. X_5 in Table 2. As expected, n_D of the oligomer and of the cured film were increased as the amount of aromatic groups in the thiol compound was increased (cf. X_3 vs. X_4 in Table 2). Further, alkyl groups usually lead to lower n_D of polymers due to a decrease in polarizability.⁴ In fact, X_6 , which has very similar structure to X_2 except the presence of the methyl substituent in thiol, has lower n_D (cf. Table 2.)

Table 2. Molecular weight and n_D of melamine acrylates and thiol adducts

Oligomer	\overline{M}_w	P_d	BMA	Thiol	n_D^a (oligomer)	$n_D^{a,b}$ (film)
BMA-222	1000	1.20	–	–	1.512	1.522
BMA-224	1100	1.23	–	–	1.512	1.521
X_1	1200	1.34	BMA-224	Thiophenol	1.566	1.578
X_2	1000	1.28	BMA-222	Thiophenol	1.552	1.559
X_3	1200	1.31	BMA-224	2-Mercaptothiazoline	1.589	1.605
X_4	1300	1.37	BMA-224	2-Mercaptobenzothiazole	1.593	1.610
X_5	1400	1.43	BMA-224	Triphenylmethanethiol	1.600	1.620
X_6	1200	1.35	BMA-224	<i>p</i> -Thiocresol	1.555	1.565

^aDetermination error of n_D is ± 0.002

^bCured with 1.0% PI. Thickness of the films were $\sim 100 \mu\text{m}$.

All of the melamine acrylate adducts produced transparent films after UV-cure. n_D of the cured oligomers were higher, when compared to n_D of the corresponding liquid oligomers. Oligomer X_1 is particularly interesting for industrial application due to

relatively low cost of raw materials, low color, and low viscosity (~5000 cP).

Composition of three UV-curable formulations (denoted as **F**) based on **X₁** and physical properties of the cured films **F_i** are presented in Table 3.

Table 3. Formulations (F_i) based on X₁ and mechanical properties of the cured films

	F₁	F₂	F₃	F₄
X₁^a (wt.%)	99	69	49	-
BMA-224 (wt.%)	-	-	-	49
IBOA (wt.%)	-	30	-	-
TRPGDA (wt.%)	-	-	50	50
PI (wt.%)	1.0	1.0	1.0	1.0
Viscosity ^b (cP)	5400	400	150	100
Tensile Strength ^b (MPa)	87	270	399	6700
Elongation-at-break ^b (%)	8	30	5	3.3
Tensile Modulus ^b (MPa)	1.2	2.9	51	320
Durometer Hardness ^b	74D	73D	54D	85D

^aCf. Table 2 for a composition of **X₁**

^bDetermination error is 10%

Tensile strength and tensile moduli of the films formed from melamine acrylates diminish with the thiol modification due to the consumption of acrylate bonds and possibly due to formation of non-acrylated oligomer molecules. The films obtained from **X₁** (cf. Table 2) have low tensile strength due to a low concentration of acrylate groups, **X₁** probably has lower crosslink density compared to BMA-224. Addition of more thiols to acrylates consumes the acrylate groups available for UV-cure, and hence decreases the tensile strength and toughness of the cured coatings. Therefore, there is a trade off between mechanical properties and refractive index in the approach with thiol addition. Thiol to initial acrylate molar ratio of 0.6 was selected as the optimum ratio for the

addition reactions to acrylates. Glass transition temperature T_g of the cured films would be an important film characteristic. However, Dynamic Mechanical Analysis (DMA) study of the cured films requires a special study.²¹

We have also compared n_D of addition products of aromatic isoelectronic amines and thiols. Amine modified melamine acrylates were synthesized by Michael addition according to a protocol described by Jerome et al.²² to demonstrate the effect of sulfur and nitrogen on the refractive index. BMA-224 reacted with *N*-methylaniline and 2-aminobenzothiazole. Refractive indices of the oligomers and cured films were given in Table 3. The replacement of sulfur atoms by nitrogen atoms usually leads to a decrease of n_D .⁴ That observation holds true for the synthesized new oligomers and corresponding cured films.

Table 4. Refractive index of adducts of thiols and amines to BMA-224

Thiol/Amine	n_D^a (oligomer)	$n_D^{a,b}$ (film)
Thiophenol	1.566	1.578
<i>N</i> -Methylaniline	1.538	1.547
2-Mercaptobenzothiazole	1.593	1.610
2-Aminobenzothiazole	1.530	1.537

^aDetermination error of n_D is ± 0.002 .

^bCured with 1.0% of PI. Thickness of the films was ca. 100 μm .

Thiourethane acrylates. A number of thiourethane acrylates were prepared by a reaction of thiols or polysulfide with aromatic isocyanates. The reaction products, which had residual isocyanate groups, were capped with HEA. In general, polythiourethanes exhibit high tensile strength and excellent abrasion resistance.^{23,24} Moreover, polysulfide based thiourethanes demonstrate good oil resistance.²⁵ The typical chemical structures of the synthesized products were presented in Figure 5.

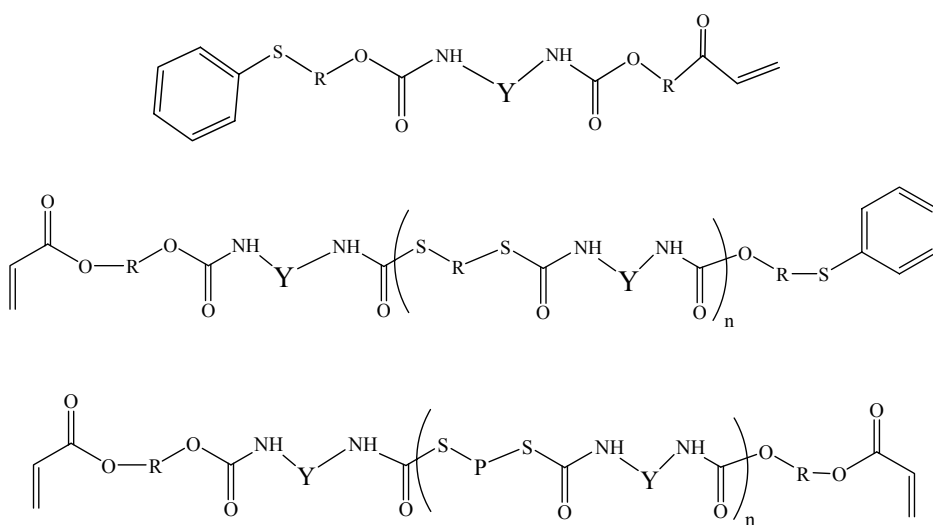


Figure 5. Generic structures of prepared thiourethane acrylates. Y stands for aromatic group, R stands for alkyl, and P stands for polysulfide, cf. the Reagents section above.

Refractive indices of the synthesized thiourethane acrylate oligomers were between 1.575 and 1.615. n_D of thiourethane acrylate oligomers increased by 1-4 % after the UV-cure of formulations **F-4** and **F-5**, cf. Table 5. The highest n_D of the obtained films was 1.66. Among these oligomers, polysulfide based thiourethane acrylate (PSTA) was particularly interesting due to high n_D , flexibility of its cured films and low cost of raw materials (cf. Table 5.)

Table 5. Mechanical properties of polysulfide-thiourethane acrylate (PSTA)

	F-4^a	F-5^a
PSTA (wt.%)	69	49
IBOA (wt.%)	30	-
TRPGDA (wt.%)	-	50
PI (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	74D	91D

^aDenotes a formulation

^bDetermination error is 10%

We can compare some properties of thiourethane acrylate oligomers and thiol-modified melamine acrylates (**X**). Thiourethane acrylate oligomers have much higher viscosities than **X**. (Thio)urethane oligomers have N-H...O=C hydrogen bonds, and their high viscosity is expected.^{20,22} Thiourethane acrylates can be obtained from different raw materials, whereas synthesis of **X** require aromatic thiols. Unfortunately, thiourethane

oligomers usually turn out to be colored which limits their industrial application. In particular, PSTA oligomers prepared in the present work have good properties (cf. the previous paragraph). Unfortunately, commercially available polysulfides have yellow reddish color, which translates into yellowish color of PSTA oligomers.

Conclusions

Novel UV-curable thioether and thiourethane oligomers were synthesized with the goal of manufacturing high n_D coatings. Nucleophilic character of thiols RS-H allows synthesis of C-S bond containing molecules. Oligomers with sulfur atoms and aromatic radicals in their structures demonstrated high n_D . This effect is expected, cf. ref. 4 for discussion. Reactions of melamine acrylate resins with aromatic thiols led to a new family of oligomers with high refractive index. Among the oligomers synthesized, **X₁** seems the most promising because it has low viscosity, can be synthesized from readily available commercial raw materials, and its formulations produce colorless films upon UV-cure. Such UV-cured films based on the new oligomers can be protective coatings for plastics. Due to their high n_D the oligomers prepared in this work can find application in radiation-curable AR coatings.

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