

New Classes of Photopolymerizable Monomers and Oligomers: Acrylamides, Urea Acrylamides and Carbonate Acrylates

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Abstract

Two new classes of potentially photopolymerizable oligomers, urea acrylamides and carbonate acrylates, were synthesized and characterized. The oligomers were added to several formulations to determine compatibility. The compatible formulations were then photocured and physically tested for adhesion, hardness, and chemical resistance. The formulations incorporating the urea acrylates and carbonate acrylates were physically compared to a standard formulation. The presentation will provide further formulation studies and comparisons.

1. Introduction

Currently in the photopolymer market, two of the largest monomer suppliers have a wide variety of photopolymerizable monomers; however, their product lines primarily comprise acrylates, methacrylates, ester acrylates, ester methacrylates, urethane acrylates, and urethane methacrylates. While these monomers produce polymers with superb physical properties for specific and varied application, by no means have all the possibilities for photopolymers been exhausted. Thus, photopolymerizable monomers incorporating a number of different functionalities need to be designed to facilitate further growth of the industry. Photopolymers may provide a viable, energy efficient alternative to traditional thermally-cured polymers with peculiar structure-property relationships.^{1,2}

Two easily synthesized alternatives include acrylamido polyureas and acrylic polycarbonates. Multifunctional acrylamides would yield, upon polymerization, a very durable and strong Nylon-like polymer which should enhance the toughness, hardness, chemical resistance, adhesion, scratch resistance, and a plethora of other properties. Polyureas are extremely durable, tough compounds and are used as substitutes for polyamides due to their higher melting points and increased resistance to abrasion. Often chemically resistant, polycarbonates are tough, transparent plastics which comprise products such as compact discs, shells on athletic helmets, shatterproof glass, and medicinal instruments. The use of these monomers could yield polymer coatings with heretofore unexplored chemical properties by simply altering the structures.

Our research herein involves the design, synthesis, and characterization of a number of photopolymerizable monomers. Specifically in this paper, the synthesis of a photopolymerizable oligomer is detailed where urea and carbonate functional groups are incorporated to produce an acrylate or acrylamide end-capped, symmetrical oligomer which could be incorporated into a photopolymerizable coating formulation. The compatibility of the oligomers in a standard

photopolymerizable formulation was also determined. Finally, the polymerized formulations, both the standard and those incorporating the oligomers, were physically tested to delineate the coatings' pencil hardness, solvent resistance, and cross-hatch adhesion.

2. Experimental

2.1 Materials

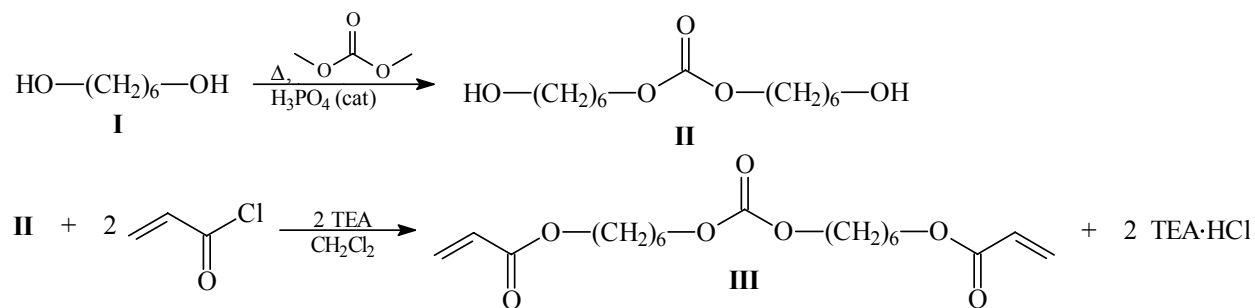
The chemicals used in the syntheses and to obtain the various spectra were all obtained from Sigma-Aldrich and included acetonitrile (ACN), acetone, acryloyl chloride, dimethyl carbonate, dichloromethane, 1,6-hexanediamine, 1,6-hexanediol, phosphoric acid, tetrahydrofuran, and N,N,N-triethylamine. The monomers used for the formulation studies, hexanediol diacrylate, a polyester diacrylate (Ebecryl 745), and trimethylolpropane triacrylate (TMPTA) were provided by Cytec Specialty Chemicals. The photoinitiator used for the formulation studies, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was donated by the Albemarle Corporation. Methyl ethyl ketone (MEK), used for solvent resistance testing, was procured from The Paint Center, a local paint store. The polished steel plates were purchased from Q Panel Products and were rinsed with acetone prior to formulation application.

2.2 Synthetic Procedures

Synthesis of 6,6'-carbonate-1,1'-hexanediol diacrylate (CHDODA).

1,6-hexanediol (0.02 mol) was dissolved in 50 mL of tetrahydrofuran (THF) while stirring. After dissolution of the diol, dimethyl carbonate (0.01 mol) was added along with two drops of concentrated phosphoric acid as a catalyst, and the solution was refluxed for six hours. After reflux, a roto-evaporator was used for isolation of the carbonate (6,6'-carbonate-1,1'-hexanediol) via the removal of excess methanol, dimethyl carbonate, and THF. 6,6'-carbonate-1,1'-hexanediol (0.01 mol) was dissolved in 25 mL of dichloromethane (DCM) while stirring. N,N,N-triethylamine (0.02 mol), TEA, was then added to solution. Following this, acryloyl chloride (0.02 mol) was slowly added dropwise under a hood to the reaction mixture immediately resulting in vigorous fuming. Once fuming ended, the reaction mixture was stoppered and left overnight while stirring. After the overnight reaction, the reaction mixture was vacuum filtered to remove all solids (TEA HCl) and washed five times (10 mL for each washing) with a saturated NaCl solution using a separatory funnel. The isolated product (dichloromethane layer) was then moved to a warm water bath to remove any excess solvent. The reaction yielded 3.10 g (83.8% yield) of a yellow liquid. IR spectroscopy was used to confirm the structure of the product, 6,6'-carbonate-1,1'-hexanediol diacrylate. The reaction scheme (Scheme 1) is shown below for CHDODA.

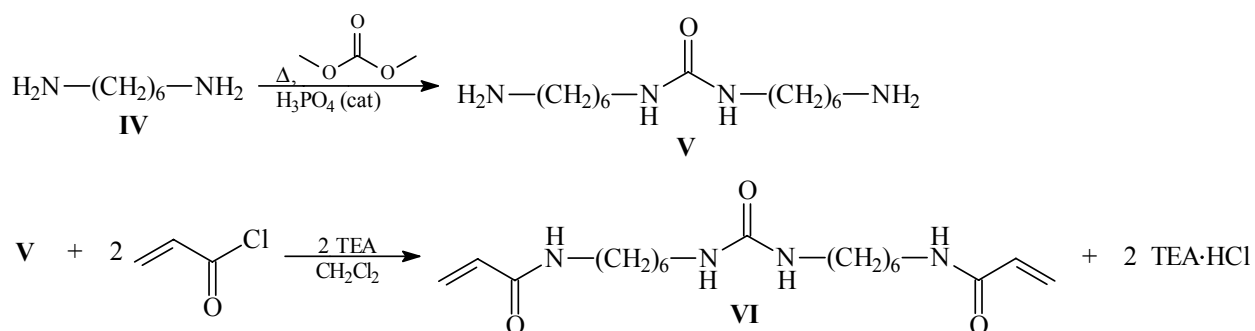
Scheme 1. Synthesis of CHDODA.



Synthesis of 6,6'-urea-1,1'-hexanediamine diacrylamide (UHDODAA).

Dimethyl carbonate (0.044 mol) was combined with 1,6-hexanediamine (0.087 mol) in 50 mL of THF, while stirring, in a 100 mL round bottom flask. This mixture was refluxed for four hours. Isolation was obtained by evaporation, first using a roto-evaporator, and then by boiling off the excess until boiling ceases. This removes excess solvent, methanol, and dimethyl carbonate. In another clean 100 mL round bottom flask, the urea intermediate (0.1 mol), 6,6'-urea-1,1'-hexanediamine, was added to a minimal volume (approximately 40 mL) of dichloromethane while stirring. TEA (0.2 mol) was added followed by acryloyl chloride (0.2 mol) was slowly added dropwise to the reaction flask causing the mixture to very vigorously fume. Once fuming ceased, the reaction mixture was stoppered and left overnight while stirring. After the overnight reaction, the reaction mixture was vacuum filtered to remove all solids (TEA·HCl) and washed five times (10 mL for each washing) with a saturated NaCl solution using a separatory funnel. The isolated product (dichloromethane layer) was then moved to a warm water bath to remove any excess solvent. At the time of writing this paper, no product large enough on which to run physical coatings tests was produced; however, enough of the product was obtained to perform a compatibility test with HDODA. The reaction scheme (Scheme 2) is shown below for UHDODAA.

Scheme 2. Synthesis of UHDODAA.

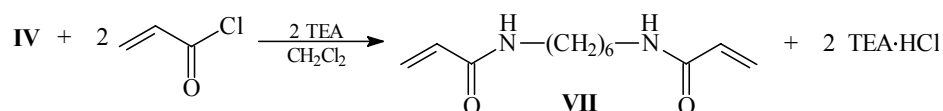


Synthesis of 1,6-hexanediamine diacrylamide (HDODAA).

In a clean 100 mL round bottom flask, 1,6-hexanediamine (0.01 mol) was added to a minimal volume (approximately 40 mL) of dichloromethane while stirring. TEA (0.02 mol) was added followed by acryloyl chloride (0.02 mol) was slowly added dropwise to the reaction flask causing the mixture to very vigorously fume. Stir for one hour, and then suction filter off the solids. Wash the remaining

liquid five (5) times with 10ml of salt water. Then take the washed liquid and reduce the volume down using a boiling water bath, controlling heat to prevent polymerization. After the cessation of fuming, the reaction mixture was stoppered and left overnight while stirring and was then vacuum filtered to remove all solids (TEA·HCl). The remaining reaction mixture was washed five times (10 mL for each washing) with a saturated NaCl solution using a separatory funnel. The isolated product (dichloromethane layer) was then moved to a warm water bath to remove any excess solvent. The reaction yielded 1.07 g (47.8% yield) of a pale yellow solid having a melting point of 127-131°C. IR spectroscopy was used to confirm the structure of the product, 1,6-hexanediamine diacrylamide. The low yield was presumed to be a result of the product's limited solubility in the saturated salt solution. The reaction scheme (Scheme 3) is shown below for HDODAA.

Scheme 3. Synthesis of HDODAA.



2.3 Infrared Spectroscopy

The IR is a Nicolet Avatar 320 which uses Fourier transform to generate the spectra. All spectra were run dissolved in acetone or acetonitrile on salt plates cleaned with dichloromethane.

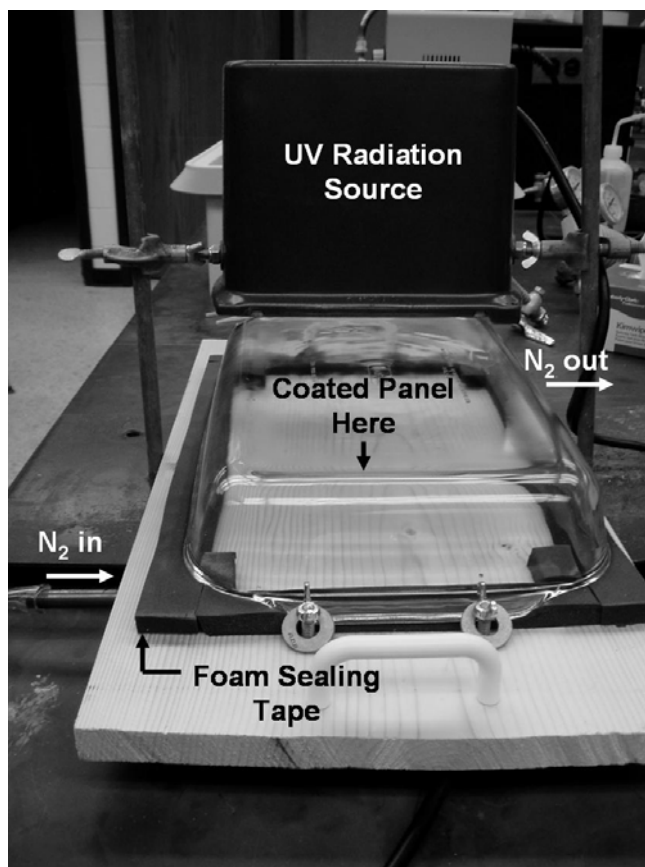
2.4 UV-Vis Spectroscopy

Absorption was measured at all wavelengths (250-450 nm) simultaneously with a Hewlett Packard Ultraviolet-Visible 8453 Photodiode Array. The desired solutions used ACN as the solvent.

2.5 Irradiation

Each formulation was applied to a polished steel plate with a thickness of four mils (100 μm) using a draw down bar and placed into a custom-made apparatus (Figure 1) designed to provide an oxygen-free environment for curing. After the lid (13" x 9" Pyrex casserole dish) is screwed down and nitrogen is allowed to purge the system for approximately two minutes, the curing apparatus is placed under the UV radiation source (Sylvania medium pressure mercury arc lamp (HPL80MDX(R) 80 Watt (R9) 0303) which had the outer casing removed). The lamp provided an intensity of 15 milliWatts/cm² at the top of the lid. The radiation intensity within the reaction chamber was not measured due to inaccuracies throughout the chamber caused by the variable thickness of the glass.

Figure 1. Custom-made curing apparatus and radiation source.



2.6 Physical Testing Procedures

All physical testing described in this paper is standardized as given hence: pencil hardness (ASTM D3363), crosshatch adhesion (ASTM D3359), and MEK double rubs (ASTM D5402-93).³⁻⁵

3. Results and Discussion

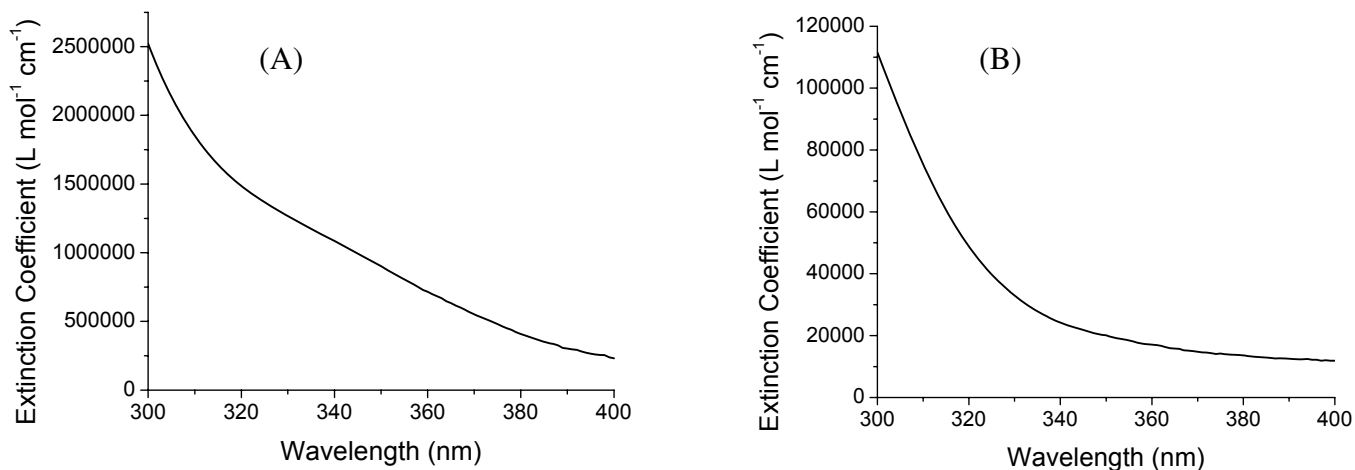
3.1 Compatibility Tests

In order to determine solubility (or compatibility) with most photopolymerizable acrylic formulations, each product (0.1 g) was mixed with HDODA for a total sample mass of one gram. The results showed that CHDODA was readily compatible at these concentrations. UHDODAA was not compatible with HDODA at these concentrations but was further dissolved to yield a compatible solution with a concentration of 0.1 weight percent when placed in a sonicator for fifteen minutes. Then, in an attempt to determine whether the solubility of UHDODAA was primarily an effect of the acrylamide or urea functionalities, HDODAA (0.1 g) was found to produce a compatibilized solution after sonication (fifteen minutes) only when diluted to a concentration of one weight percent. Thus, the urea and acrylamide functionalities seem to equally affect the compatibility of the monomer when dissolved in HDODA.

3.2 UV-Vis Spectroscopy

One of the crucial aspects of photopolymerization is that formulation (not including the photoinitiator) should not have a significant, competitive absorbance of UV radiation in the range of the photoinitiator; thus, one of the qualifying tests of any potential photopolymerizable monomer requires the acquisition of its UV-Vis absorbance spectrum. Shown below are the UV-Vis spectra of both HDODAA and CHDODA (Figure 2).

Figure 2. UV-Vis absorbance spectra of (A) HDODAA and (B) CHDODA.



Ideally, the potential monomer ceases to have any significant absorbance at wavelengths exceeding 350 nm; this behavior is highly desirable given that many photoinitiators are irradiated with wavelengths in excess of 350 nm. However, HDODAA and CHDODA had a repeatable and unexpectedly large absorbance in the range of many commercially available photoinitiators. Such large absorbances might inhibit photochemical free-radical initiation due to competitive absorbance with the photoinitiator; yet, as reported in the following section, a formulation incorporating twenty weight percent of CHDODA and only one weight percent of the photoinitiator (DMPA) was cured with low intensity UV radiation. (Curing studies with HDODAA were not attempted due to the aforementioned compatibility issues with acrylic monomer solutions.) Thus, the apparent absorbance of HDODAA and CHDODA reported herein is either aberrant, or another, as yet, unknown effect separate from the absorbance of CHDODA is increasing the efficacy of the polymerization.

3.3 Physical Testing

Only CHDODA was examined for its structure-property relationships relative to pencil hardness, solvent resistance, and crosshatch adhesion because neither HDODAA nor UHDODAA could be incorporated into a photopolymerizable formulation in concentrations large enough to provide observable differences in testing. Two formulations were made, a control and one incorporating CHDODA (Table 1). The formulation incorporating CHDODA was observed to be yellow prior to curing and after application to the substrate; however, after cure as given in the Experimental section, the coating was peculiarly without color and had photobleached. Qualitatively, it would seem that CHDODA is undergoing some sort of photobleaching reaction upon irradiation.

Table 1. Formulation compositions in weight percent.

Compound	Weight Percent in Control	Weight Percent in Test
DMPA	1.6	1.1
Ebecryl 745	18.6	19.4
TMPTA	41.5	39.8
HDODA	38.3	19.9
CHDODA	0	19.9

Table 2. Results from physical testing.

Physical Test	Control Formulation	Product Formulation
Pencil Hardness	8H	8H
Crosshatch Adhesion	Before Tape: 0 full 23 partial 2 gone	Before Tape: 0 full 13 partial 1 gone
	After Tape: 0 full 0 partial 25 gone	After Tape: 0 full 11 partial 3 gone
MEK Double Rub	200	200

After curing, three standardized physical tests were performed on each formulation in order to determine the effect of CHDODA on the coating's hardness, solvent resistance, and adhesion (Table 2). The substitution of half of the HDODA with CHDODA yielded no observable change in the hardness or solvent resistance of the coating. In fact, these results are not surprising since the curable functionalities are acrylic for both monomers. Traditionally, as was also observed herein, acrylic formulations produce superior hardness and solvent resistance. However, the formulation incorporating CHDODA was found to have better adhesion (crosshatch adhesion) than the control. Such results could be explained one of two ways. First, the carbonate functionality on CHDODA could have greater intermolecular interaction with the surface of the steel, probably as an effect of both dipole-dipole interactions and dispersion forces, than with the masking tape used. Second, the CHDODA formulation could simply be more nonpolar than the control thereby disallowing the favorable interaction of the coating with the tape and causing less of the coating to delaminate. Further varied adhesion testing could yield more definitive conclusions concerning the effect the addition of CHDODA has on the overall adhesion of the coating to the substrate; however, these preliminary tests seem to indicate enhanced adhesion for a coating incorporating some CHDODA instead of HDODA.

4. Conclusions

Three monomers were synthesized: HDODAA (an alkyl diacrylamide monomer), CHDODA (a carbonate diacrylate oligomer), and UHDODAA (a urea diacrylamide oligomer). Of the three monomers synthesized, only CHDODA was compatible when mixed with an acrylic formulation. Due to the perceived lack of solubility for the diacrylamides, CHDODA was the only monomer incorporated into a photopolymerizable formulation and subsequently cured. After curing, several standardized physical tests were performed including pencil hardness, solvent resistance via MEK double rubs, and

crosshatch adhesion. The formulation incorporating CHDODA yielded comparable hardness and solvent resistance relative to the control formulation and showed superior adhesion relative to the control.

5. Acknowledgements

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6. References

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