# High Performance Non-Traditional Acrylated Oligomers

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**Abstract**. Urethane acrylates based on polyols and epoxy acrylates are widely used traditional radiation-curable materials. The paper describes new or less-known UV-curable acrylated oligomers: acrylated phenoxy resins, multifunctional melamine acrylates with a very low free formaldehyde content, acrylated cellulosic compounds (CAB), dendritic acrylates, poly(amide imide) acrylates,  and matte acrylated oligomers with nanoclay. We present one allylic oligomer for a dual cure as well. Development of these oligomers, which meet demands of the modern coatings market, required resolution of a number of chemical problems, which are outlined in this paper.  Properties of liquid and cured coatings including their application in the industry are briefly discussed.

**Introduction.**  Urethane acrylates, oligomers based on different polyfunctional polyols, and epoxy acrylates are the most widely used oligomers in radiation-curable coatings.[1,2] We estimate that more than 50% of the world production of oligomers are urethane and epoxy acrylates. Our group is involved in research of urethane acrylates.[3-7] Other radiation-curable oligomers evidently bring other properties and can better meet customer demands in terms of performance and cost. Acrylates are the best known and most commonly used substituents or capping agents in oligomers, which undergo free-radical photopolymerization (photocure).  This paper describes a number of new or less known acrylated oligomers and one allylic oligomer, and briefly discusses their synthesis, structure and properties.  In some cases acrylation was performed through urethane (carbamate) links. Radiation-curable formulations usually include an oligomer as the main component, mixed with reactive diluent(s), and other additives.[1,2] We performed  a photocure with UV-light formulations, which had oligomer(s), 30-50 wt.% of a diluent and a few wt.% of a common Type I photoinitiator[1] (PI). We discuss these oligomers below.

**Acrylated cellulose derivative.** Acrylation of cellulose acetate butyrate (CAB) with aqueous *N*-(hydroxymethyl)acrylamide solution through a proprietary process leads to very high molecular mass (MW) acrylated oligomer (or a low MW polymer):

**REAGENTS**
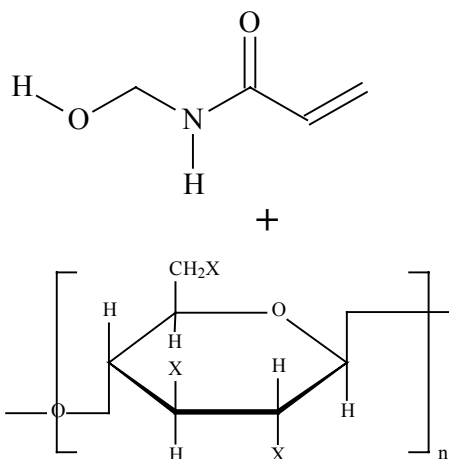


*N*-(hydroxymethyl)acrylamide

**Attached Groups**
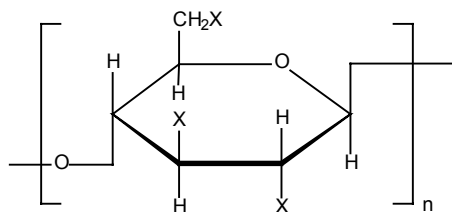
celluose—OH    Hydroxyl

celluose—O—C(=O)—CH₃    Acetyl

celluose—O—C(=O)—CH₂CH₂CH₃    Butyryl

Cellulose, acetate butanoate (CAB)

X can =
= Hydroxyl
= Acetyl
= Butyryl

**PRODUCT**

**Attached Groups**

celluose—OH    Hydroxyl

celluose    Acetyl

celluose    Butyryl

celluose    Acrylamidomethyl

X can =
= Hydroxyl
= Acetyl
= Butyryl
= Acrylamidomethyl

Cellulose, acetate butanoate, [(1-oxo-2-propenyl)amino]methyl ether

**Scheme 1**

The product has a name of **Jaylink™**; **Jaylink™** 103M, $M_w$ = 50,000 and **Jaylink™** 106E, $M_w$ = 56,000 g/mol. The materials are soluble in most organic solvents, and acrylic monomers (diluents) can dissolve up to 30% **Jaylink™.**

 **Jaylink™** is as UV-curable cellulosic. One of its common uses is as reactive thickener and thixotrope for UV-curable formulations.

Usually **Jaylink™** is added into formulations at a relatively low concentration of 2-10%. Along with being a thickener, **Jaylink™** often improves adhesion, increases tensile strength, impact resistance, solvent resistance, toughness, and gloss. In ink application, the rheological properties of additive **Jaylink™** serve to prevent the ink from wicking into porous substrates (swo-called "ink-drying".) Formulations with **Jaylink™** usually have higher rates of photocure than similar formulations without **Jaylink™**.

Still, the modest solubility of **Jaylink™** can create problems. In order to add **Jaylink™** to a formulation, one selects a monomer (reactive diluent) of the strongest solvency out of monomers to be used in the formulation. It is recommended tostir the diluent with a high shear mix blade and heats the diluent up to ~ 60 °C. Sifting of **Jaylink™** into the vortex of the monomer prevents agglomeration.

**Jaylink™** synthesis seems to be a simple one-step reaction, cf. Scheme 1. However, one starts with a white powder, gets a heterogeneous aqueous mixture, and ends up with a white powder again. It is not trivial to avoid agglomeration in this process.

**Phenoxy Resin.** Phenoxy resin is comprised of high MW polyhydroxy ethers built from bisphenol A and epichlorohydrin via linear addition; cf. Scheme 2. (InChem Corp manufactures this
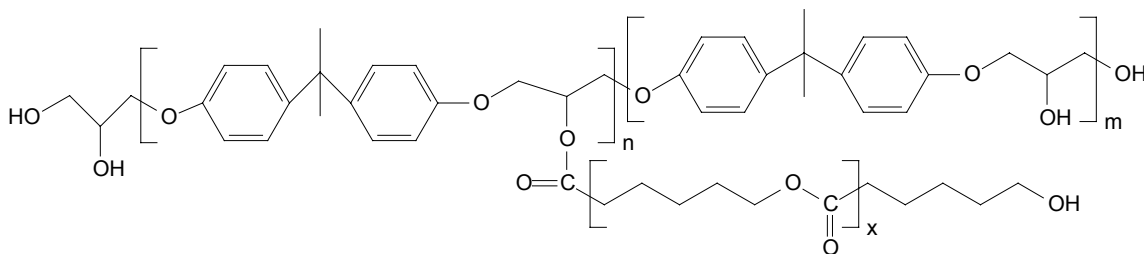


**Scheme 2**

resin.[8]) We acrylated the phenoxy resin with diisocyanate (TDI) and 2-hydroxethyl acrylate (HEA):
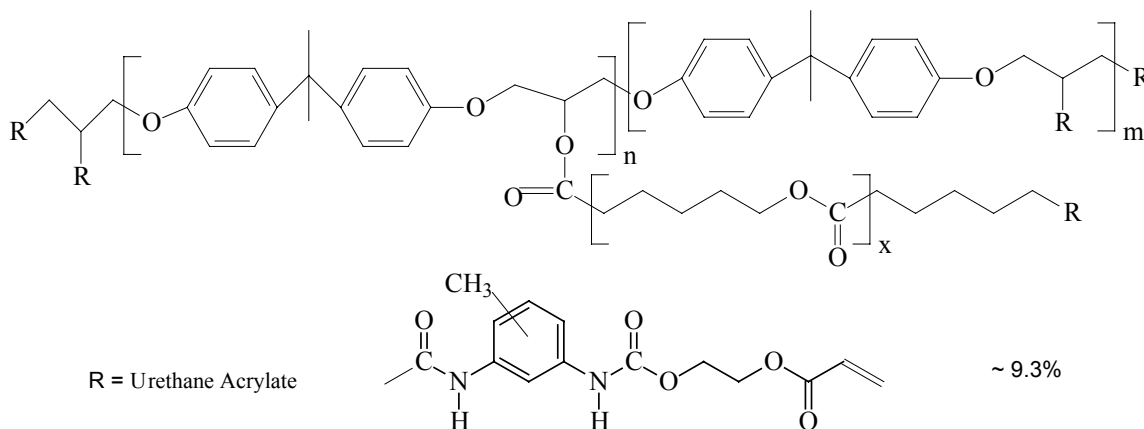


R = Urethane Acrylate          ~ 9.3%

or:

R = Hydroxyl Group     —OH     ~ 91.7%

**Scheme 3**

Scheme 3 above presents the chemical structure of phenoxy urethane acrylate resin, which was given a common name or abbreviation **BRP**.

Unlike conventional oligomers, properties of cured **BRP** are due to the initial properties of the base backbone. In addition, the high performance of **BRP** is a result of the crosslinking (photopolymerization). There are three key formulating elements of interest for **BRP**:

1) Diversity of adhesion. **BRP** demonstrates goodt adhesion across a wide array of plastics and metals. Particularly, when diluted in monofunctional monomers (acrylates), the base resin demonstrates outstanding adhesion to metals such as aluminum, cold rolled steel, stainless steel, brass and other copper alloys, and zinc. **BRP** has a good adhesion to plastics with any degree of polarity or functionality or relatively high surface tension: PVC, acrylic, polycarbonate, polyester film, polystyrene, ABS, etc. In short, adhesion can be expected to any substrate other than polyethylene or polypropylene-based systems.

2) Very low shrinkage. Due to its high $M_w$ (at least 36,000 g/mol) and low functionality, **BRP** does not shrink observably upon cure. Pre- and post-cure dimensional stability of this contributes to the adhesion benefits of **BRP**, but can be of additional benefit in many applications sensitive to volume changes during photopolymerization.

3) High chemical resistance. Phenoxy backbones are similar to those of bisphenol A epoxies (and epoxy acrylates derived from the same), and exhibit the similar strong chemical resistance, but with more flexibility.

**BRP** finds the main application in clear coatings and hard/rigid adhesives.


**Matte oligomers.** There is a great interest in nanotechnology and in nanocomposites in particular. However, we, as some other researchers,[9] did not observed the expected profound improvement of mechanical, physical or chemical properties of coatings upon addition of 1-10 wt.% of nanoparticles or nanoclay. In agreement with many observations (cf., e.g., ref. 9), we noticed that an addition of nanoparticles or nanoclays does not decelerate photocure of coatings. One application of nanoclay turned out to be rather useful. An addition of montrillomonite functionalized with quaternary amine to many oligomers including "traditional" urethane acrylates led to a formation of matte oligomers. The latter are valuable in different applications and especially in furniture wood coatings.

Cure of trifunctional urethane acrylate oligomer **A**[10] blended with 50% tripropylene glycol diacryalte (TRPGDA, 50 wt.%) and PI led to an abrasion resistant hard coating. A liquid formulation had viscosity $\eta = 1200$ cP at 25 $^0$C. The cured formulation had average 90 gloss units (GU) measured at $60^0$. A similar formulation with the same oligomer **A,** containing 10.7% of nanoclay and designated as **A-N,** mixed with the same relative amount of TRPGDA and having the same concentration of the same PI as in the formulation with **A,** had even lower $\eta = 990$ cP at 25 $^0$C. Cured formulation with **A-N** had average 17 GU measured the same way. One can matte **A-N** to a dead flat finish with a small (1-5%) addition of fumed silica, resulting in matted systems of much lower $\eta$. Such dead flat finish was previously impractical to apply.

**Crosslinking oligomer for a dual cure.** It is well known that dioxygen inhibits free-radical photopolymerization.[1,2] One often observes a sticky or greasy surface of coatings after UV-cure in the air ("poor surface cure"). Hydroperoxides of a generic structure ROOH are present in the top layer. It was suggested to use a detrimental $O_2$ effect to an advantage of the user. Monsanto and Solutia came up with an allylic oligomer, namely polyallyl glycidyl ether, which is easily oxidized by air $O_2$.[11] Inventors assigned a name **XI-100** to the oligomer.[11] The structure of **XI-100** is presented below (Scheme 4):[11]
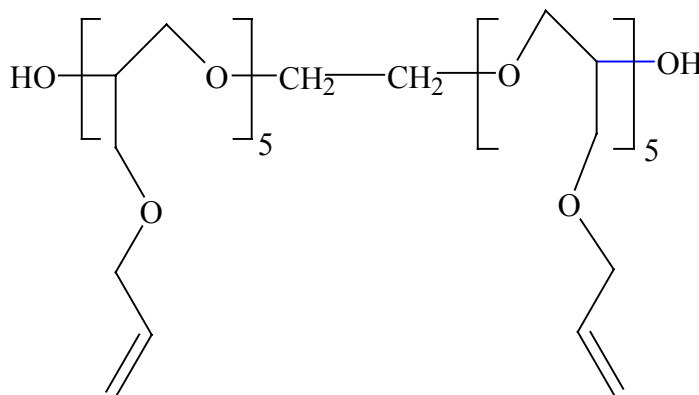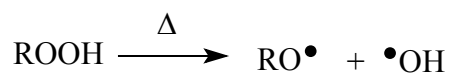


**Scheme 4**

**XI-100**, which has allylic C-H bonds of low bond dissociation energy (BDE), oxidizes by air $O_2$ with a formation of ROOH (Scheme 5):
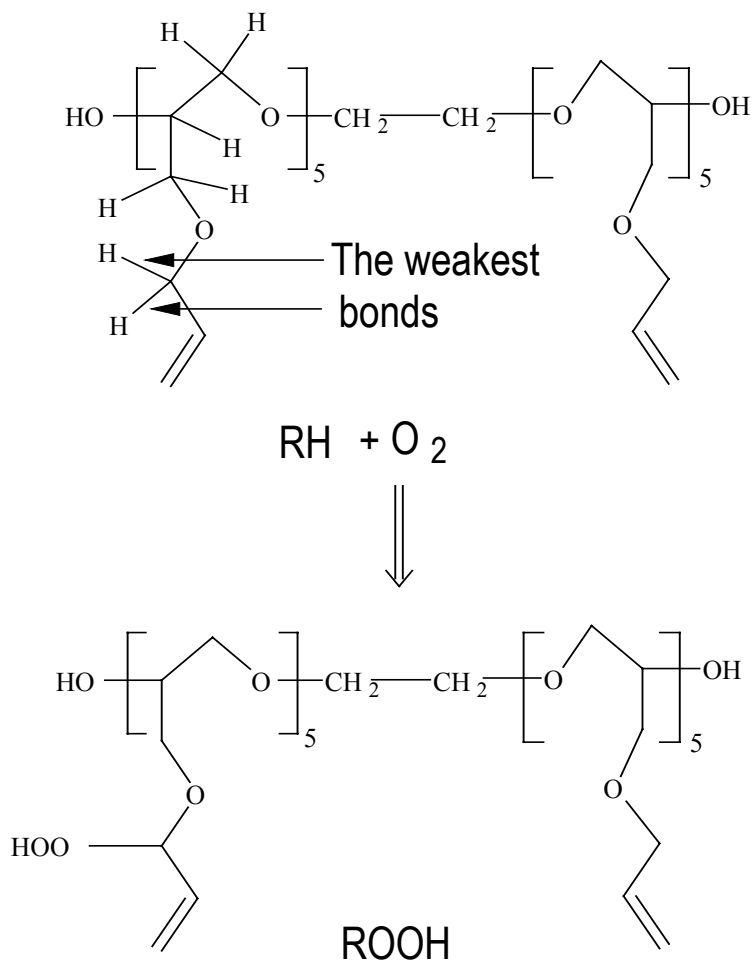
**Scheme 5**

Accumulated ROOH decomposes at room or at elevated temperature and initiates polymerization in the surface layer, shadowed areas or in deep layers of coating:

$$ROOH \xrightarrow{\Delta} RO^{\bullet} + {}^{\bullet}OH$$

Free-radical decomposition of ROOH occurs much faster at higher temperatures or in the presence of so called "metal driers" [12], i.e., salts or compounds of transition metals $Me^{n+}$, which decompose ROOH acting as catalysts. The reaction below represents decomposition catalyzed by a metal drier:

$$2\ ROOH \xrightarrow{Me^{n+}} RO^{\bullet} + RO_2{}^{\bullet} + H_2O$$

Alkoxyl radicals $RO^{\bullet}$ initiate dark polymerization.

We performed a catalytic synthesis of **XI-100**, and gave a name of **BXI-100** to the product. **BXI-100** becomes lightly colored despite the lack of oxidizing agents during synthesis. Efforts are required to minimize the color.

It was noticed recently that such environmentally friendly compound as ascorbic acid reduces ROOH with a formation of reactive free radicals.[13] Thermoinitiators (peroxides, azo-compounds, etc.) evidently accelerate polymerization of formulations containing **BXI-100**.

It is recommended to add **BXI-100** of a low level of 5-15 wt.% to UV-curable formulations. A system should absorb an *optimal amount* of $O_2$, enough to from a certain concentration of ROOH and not excess in order to be left dissolved or to create too much of ROOH. In order to avoid excessive consumption of $O_2$, the system is sealed at the top layer by the usual UV-cure.

**BXI-100** will initiate polymerization in *shadowed areas* or in *deep layers* of a coating, or in *pigmented layers* of coatings uncured by UV-light. **BXI-100** will improve "surface cure" as well. Activators of **BXI-100** mentioned above accelerate dark cure.

Potential applications of note include field-applied concrete and wood refinish products, along with OEM automotive coatings, and other applications with complex substrate topology.

**Dendritic acrylates**. A family of dendritic or hyperbranched polyols are commercially available.[14,15] Esterification of a number of OH groups of dendritic polyols with acrylic acid leads to UV-curable dendritic acrylates, Scheme 6:
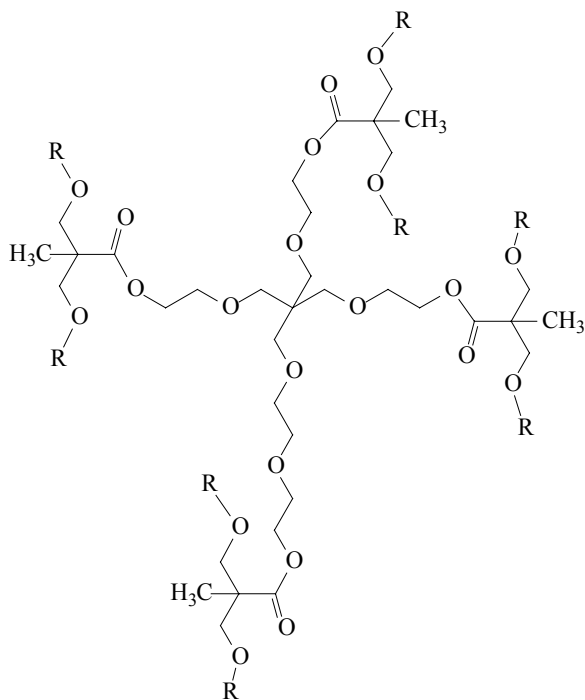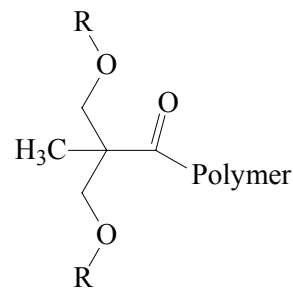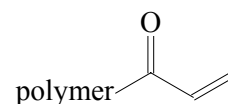


**Scheme 6**

These dendritic acrylates compounds (a given designation is **BDE**) are characterized by relatively low viscosity η (for a high MW oligomer) due to their nearly

spherical structure, which minimizes entanglement of oligomeric molecules. We acrylated not individual dendritic polyols but binary mixtures of polyol with trifunctional polyether alcohols, where polyol is more than half of a mixture. We prepared two different **BDE** products with average acrylate functionality of eight and fourteen and with free residual OH groups of hyperbranched polyol.

The cure of star-like molecules leads to low shrinkage. Low MW diluents in dendritic acrylates help not only reduce $\eta$ but increase the degree of cure, allowing higher mobility in a formulation and most probably reducing $T_g$.[16]

Two synthesized **BDE** demonstrate high abrasion resistance. They can be formulated to have reasonable flexibility for a hard cured film. The high crosslink density leads to a chemically resistant film that still exibits good adhesion to selected substrates.

Dendritic polyols can also be acrylated through urethane (carbamate) links.[17] Diisocyanate reacts with $\omega$-hydroxyalkyl acrylate and subsequently reacts with dendritic polyols (reverse addition[3]). We prepared a number of dendritic urethane acrylates, but abundance of hydroxyl groups makes a synthesis difficult as a batch easily gels. Properties of dendritic urethane acrylates are beyond the scope of this paper.

**Melamine acrylates.** Melamine resins are well known in the coatings industry.[2] Our goal was to make available for us melamine resins UV-curable. We reacted the resin with 2-hydroxyethyl acrylate (HEA). Acrylated melamine resins were designated as **BMA**. Scheme 7 below presents a structure of trifunctional **BMA**:
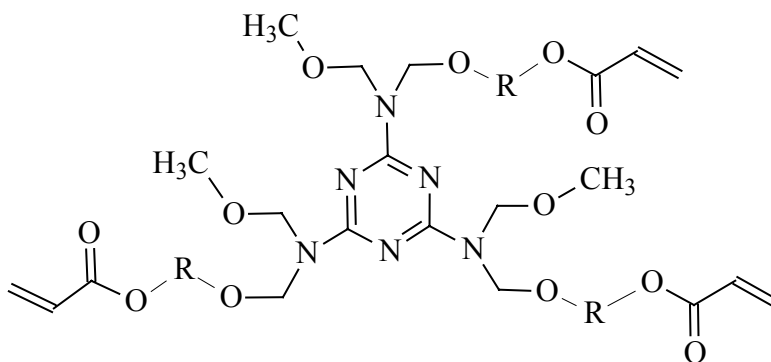


**Scheme 7**

Synthesized **BMA** have relatively low $M_w < 2,000$ g/mol and a relatively low viscosity $\eta$. Although the melamine resin has been functionalized, the resin still contains much of the melamine properties.

We observed that **BMA** cures faster than urethane acrylates of the same functionality, and **BMA** requires much less amount of photoinitiator (PI) in order to reach cure. For example, we cured trifunctional urethane acrylate and trifunctional **BMA** with PI Irgacure 184**.** Oligomers were of comparable $M_w$, and each oligomer was diluted twice with a diluent, cf. Table 1.

Table 1

**Properties of trifunctional melamine acrylate and trifunctional urethane
acrylate diluted with 50 wt.% of TRPGDA at 25 $^0$C**

| | BMA-222[7] | BR-144[7] |
|---|---|---|
| $\eta$, cP[a] | 100 | 1050 |
| Tensile modulus, MPa[a] | 14.1 | 25.2 |
| Elongation-to-break, %[a] | 15.2 | 10.6 |
| Durometer hardness[a] | 77D | 82D |
| Passes at 20 ft/min[b] | 3 | 3 |
| PI, wt.% | 0.1 | 2.0 |

[a]Determination error is 15%
[b]Samples were cured in the air with Fusion D bulb, 300 W/in

The major difference between **BMA-222** and **BR-144** in this example is the concentration of PI: **BMA-222** can be cured with *extremely low concentration of PI.* (It is 20 times lower compared to urethane acrylate).

Many melamine resins have an unpleasant smell of formaldehyde.[2] Mineral or organic acid is used in a standard dark cure (condensation) of melamine resins, which is accompanied by demethyolation and by an additional release of formaldehyde. Acid-catalyzed reaction of melamine resin with HEA, which is an alcohol, also leads to a formation of HCHO. We have selected catalytic system, which, contrary to many other catalysts, result in a clear, not a turbid resin. An addition of a proprietary base terminates equilibrium reactions in acidic solutions containing melamine, and therefore brings to a halt any further evolution of free formaldehyde. The remaining free formaldehyde is stripped. There is a dramatic difference in a level of formaldehyde before and after neutralization:

| | Standard catalyst[a] | Proprietary catalyst[a] |
|---|---|---|
| Free formaldehyde, mass fraction | 10000 ppm | 270 ppm |

[a]Determination error is 15%

According to many users, **BMA-222** does not smell formaldehyde. In addition to reducing free HCHO in the final liquid resin, the neutralizing agent leads to an increase of shelf stability of **BMA**. Acid-induced condensation of melamine resins, which leads to an increase of their $\eta$ an eventually to gelation, is prohibited in **BMA** due to lack of free acid. **BMA-222** is used in particular in the furniture industry.

**Acrylated poly(amide imide).** Aromatic polyimides are extremely thermally stable polymers with good mechanical properties. In order to improve their processability, a number of attempts were made to prepare mixed polymers (oligomers) with incorporation of flexible segments into polyimides[18] and even make such oligomers UV-curable.[19] Similarly, implementation of imide or other rigid cyclic fragments into flexible polyurethanes improves heat resistance of polyurethanes.[20,21] We prepared UV-curable

acrylated oligomeric amide imide or poly(amide imide). We used a reaction between a cyclic anhydride of aromatic diacid or maleic ahnydride and isocyanate group leading to imide as the main product of the synthesis.[21,22]

We reacted benzene-1,2,4,5-tetracrboxylic acid dianhydride (PMDA) and diisocyanate (IPDI). Reaction product was endcapped with so-called "caprolactone acrylate" (Tone M100 of Dow). As a result we obtained UV-curable *imide* oligomer of a simplified structure: **Tone-(IPDI-PMDA-IPDI)$_n$-Tone**, cf. Scheme 8:
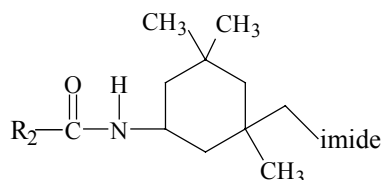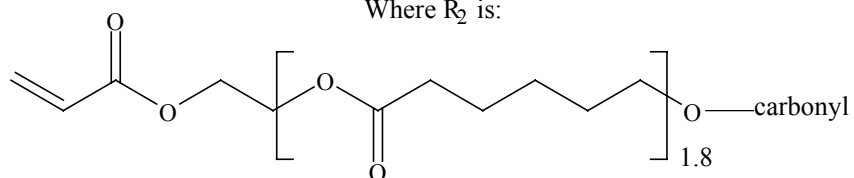


Where R is:
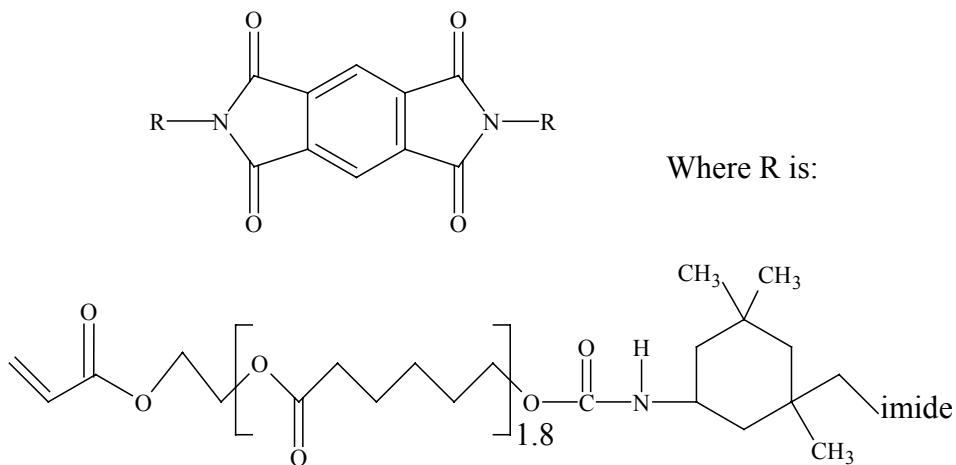


**Scheme 8**

(1.8 is an average number of repeating units in the used Tone M100.) Reaction is accompanied by formation of other oligomer(s) and by release of $CO_2$. In particular, Tone M100, which is an alcohol, reacts with PMDA with a formation of ester and acid. The acid reacts with IPDI with a formation of *amide*, cf. Scheme 9: [19,23]
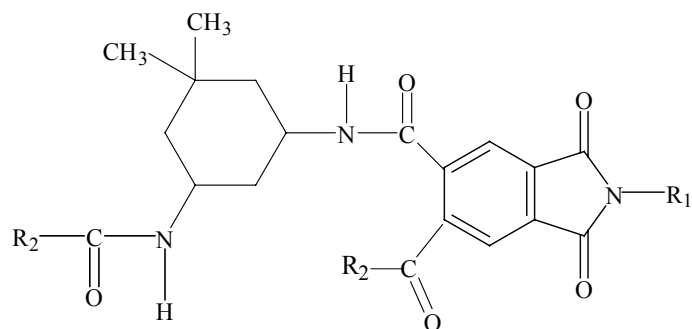
Where R₁ is:



Where R₂ is:



**Scheme 9**

We ascribed a designation to this blend of oligomers as **XRI-PMDA**. The composition of oligomers depends upon reaction conditions and ratio of inputs. **XRI-PMDA** presents an interesting balance of properties including heat resistance provided by imide fragment, and adhesion affinity for polyimides and similar materials, along with the beneficial toughness and high rates of UV-cure typical of a urethane acrylate.

Acrylated poly(amide imide) can be used for pigment wetting and grinding, and so is suitable for consideration in offset and screen-print ink applications. High temperature performance and electronics properties of this product are under investigation.

We prepared oligomer similar to **XRI-PMDA**, where we used instead of PMDA bezophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA, Scheme 10) in the same molar amount.
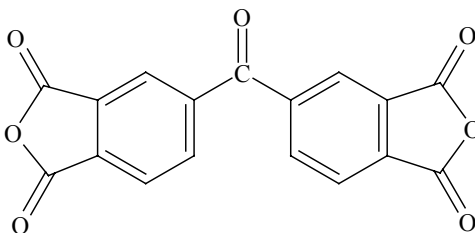
**Scheme 10**

We designated that oligomer **XRI-BTDA.** For a sample **XRI** with PMDA we got $M_w$ = 1670 and for a sample with the same molar amount of BTDA we got $M_w$ = 2550 g/mol.

It is easy to notice, that BTDA has benzophenone fragment. Benzophenone is a well-known Type II PI, which initiates photocure in the presence and even in the absence of coinitiators.[1] Evidently, benzophenone fragment is preserved in **XRI-BTDA**. We have found that **XRI-BTDA** oligomer *is self-curable.* That means that UV-irradiation of **XRI-BTDA** *in the absence of any PI in the air leads to photocure in a thin layer.* (Apparently **XRI-BTDA** has a very high concentration of PI, which is a segment in oligomer chains. BTDA fragment and products of its reaction absorb UV-light, they do not bleach under UV-light. That explains a cure in thin layers.) Addition of reactive diluents to **XRI-BTDA** allows obtaining a deeper cure.

*Self-curable* of *self-initiating UV-curable* systems are very rare, and they are of much academic and practical interest.[24-28]

We are not in a position to study photochemistry of BTDA and of liquid **XRI-BTDA**. We speculate that benzophenone fragment in n,$\pi^*$ excited triplet state abstracts hydrogen from alkyl groups of **XRI-BTDA** and forms reactive alkyl radicals.

# Conclusions

. We outlined in the paper high performance acrylated oligomers and presented their idealized chemical structures. Formulations were cured with UV-light in the presence of PI, but oligomers can be used in EB or other radiation-curable formulations with similar expected results. We demonstrated that there is almost always a way to attach acrylate group to one or another oligomer backbone and to get eventually a desired cured polymer in the course of free radical photopolymerization.

All efforts should be taken to reduce color of the final oligomers. When possible, a reaction should be run at relatively low temperature in the inert atmosphere with a proper catalyst. Most of our reactions were solventless.

There are probably less than ten different reactive groups tethered to oligomers, which are used in radiation-cure technology, and (meth)acrylate group is the most common.[29] We discussed only acrylated oligomers in this paper; methacrylated versions of oligomers are either available, or they can be prepared in similar reactions.

Reactions of anhydrides with acrylated alcohols or with isocyanates are known, but they are not much exploited in industry as a route to new oligomers. Such reactions, of cyclic anhydrides leading to maleimides and other photocurable oligomers, deserve further study.

In certain cases one-pot synthesis leads to more than one oligomer, and that is not necessarily bad. New products like **XRI**, which is a mixture of oligomers, demonstrate valuable properties. Self-initiation of **XRI-BTMA** is a rare interesting phenomenon in coatings with promising practical applications.

High performance oligomers presented in this paper provide a favorable balance of properties and processability. More detail on the oligomers discussed in this paper can be found elsewere.[7]

# References

1. Fouassier, J.-P. *Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications*; Hanser: Munich, 1995.
2. Wicks, Z.W.; Jones, F.N.; Pappas S.P. *Organic Coatings*; Wiley: New York, 1999.
3. Swiderski, K.W.; Khudyakov I.V. *Ind. Eng. Chem. Res*. **2004**, *43*, 6281.
4. Khudyakov, I.V.; Swiderski, K.W.; Greer R.W. *J. Appl. Polym. Sci.* **2006**, *99*, 489.
5. Leon, J.A.; Khudyakov, I.V.; Zopf, R.D. 2005, In *RadTech Asia*, p. 243.
6. Khudyakov, I.V. *Paints & Coat. Ind.* **2004**, March, p. 52.
7. www.bomarspecialties.com
8. www.phenoxy.com
9. Uhl, F.M.; Davuluri, P.; Wong S.-C.; Webster D.C. *Polymer* **2004**, *45*, 6175.
10. We present here data for a common urethane acrylate **A** as an exception, focusing on matting properties of nanoclay. Nanoclay is reactive towards diisocyanates; that problem should be addressed.
11. Knapszyk, J.W. *J. Coat. Technol.* **1988**, *60*, 63.
12. The history of metal driers can be traced back to the easel paintings of Dutch artists of 15 century, cf. Perkins, M.J. *Radical Chemistry*; Ellis Horwood: New York, 1994, p. 120.
13. Steinert, A. *Europ. Coat. J.* **2005**, *#3*, 84.
14. Hyperbranched polyols of Perstorp have a common name of Boltorn®, cf. www.perstorp.com
15. These are not *dendrimers.* Dendrimers are monodisperse and perfectly branched macromolecules.
16. Khudyakov; I. V.; Purvis M.B.; Turro, N. J. In *Photoinitiated Polymerization*; Belfield, K.D.; Crivello, J.K., Eds; ACS Symposium Series 847; American Chemical Society, Washington, DC, 2003, p. 113.
17. Tasic, S.; Bozic, B.; Dunjic, B. *Prog. Org. Coat.* **2004**, *51*, 320.
18. Mehdipour-Ataei, S.; Hatami, M. *Europ. Polym. J.* **2005**, *41*, 2010.
19. Su, W.-F. A. US 5,206,381.
20. Takeichi, T.; Ujiie, K.; Inoue, K. *Polymer* **2005**, *46*, 11225.
21. Liao, D.C.; Hsieh, K.H. *J. Polym. Sci. A.* **1994**, *32*, 1665.
22. Sendijarević, A.; Sendijarević, C.; Frisch, K.C., et. al. *J. Polym. Sci. A.* **1990**, *28*, 3603.
23. Alvino, W.M.; Edelman, L.E. *J. Appl. Polym. Sci*. **1978***, 22*, 1983.
24. Khudyakov, I.V.; Fox, W.S.; Purvis, M.B. *Ind. Eng. Chem. Res*. **2001**, *40*, 3092.
25. Gould, M.L.; Narayan-Sarathy, S.; Hammond, T.E.; Fletcher, R.B. 2006, In *RadTech Europe,* v. 1, p. 245.
26. Decker, C.; Bianchi, C. *Polym. Int* **2003**, *52*, 722.
27. Lee, T.Y.; Roper, T.M.; Jönsson, E.S.; Khudyakov, I.V.; Viswanathan, K.; Nason, C.; Guymon, C.A.; Hoyle, C.E. *Polymer* **2003**, *44*, 2859.
28. Hoyle, C.E.; Lee, T.Y.; Wei, H.; Guymon, C.A.; Jönsson, E.S. 2006, In *RadTech Europe,* v. 2, p. 17.
29. Miller, C.W. *RadTech Report* **2005**, *#7/8*, 52.