# UV Curable Ink Jet Raw Material Challenges

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## Abstract

Radiation curable ink jet printing is rapidly developing new technology for digital imaging. The strict property requirements of an ink jet ink formulation in terms of viscosity, cure speed, cured film performance, pigment wetting and friendly EH&S profile present many challenges to the ink formulator and the supplier of radiation curable raw materials. Traditionally radiation cured inks and coatings have used relatively high molecular weight/high viscosity oligomers to acheive properties. The presentation will cover properties and performance aspects of monomers and oligomers suitable for radiation curable ink jet systems. A main focus will be on a new family of low-viscosity/high functionality polyester acrylates that address many of the performance issues noted above.

## Introduction

UV curable ink jet printing is a rapidly developing area of digital imaging for industrial applications. The advantages of UV curing now recognized in coatings, adhesives and other types of inks are becoming available to the ink jet market. These advantages include no or very low VOC emissions, fast cure, low energy requirements, superior physical properties and the ability to tune in a wide range of physical properties.

Ink jet printing presents some unique challenges to the suppliers of radiation curable raw materials in terms of achieving in the same molecule the liquid properties needed for jetability and drop formation and the print and film properties required after curing.

**Liquid Properties:**

- Low Viscosity
- Low Volatility
- Friendly EH&S Profile
- Good Droplet Formation
- Formulation Stability
- Fast Cure

**Cured Properties:**

- Scratch/Abrasion Resistance
- Adhesion to Substrates
- Hardness
- Flexibility
- Good Color Density
- Sharpness of Image

UV curable formulations typically consist of mixtures of acrylated monomers and oligomers. The monomer's role is to reduce viscosity, provide crosslinking and contribute some physical properties. The oligomer provides the bulk of the physical properties of the final cured film and in the case of inks provides stability of the pigment dispersion. The common epoxy acrylate, urethane acrylate, polyester acrylate, acrylated acrylic or other oligomers usually used in UV curable formulations are of too high viscosity to be used at any more than a few percent concentration in an ink jet formulation. In most cases this is not enough to achieve desirable physical properties.

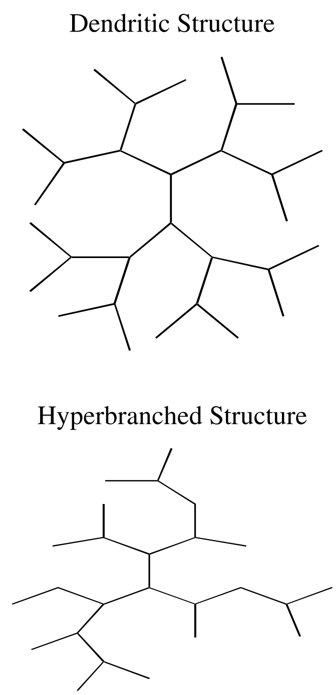


*Figure 1. Dendritic and Hyperbranched Structures.*

## Dendrimers and Hyperbranched Polymers

In contrast to linear polymers and oligomers dendrimers are characterized by structures that are densely branched, are approximately spherical in shape and have a large number of end groups. From an industrial standpoint one drawback of dendrimers is that their highly regular structures require they be made by multi-step repetitive synthesis techniques resulting in high cost. Hyperbranched polymers are similar to dendrimers, but have less regular, well-defined structures and are more amenable to industrially attractive synthesis techniques. Dendrimers and hyperbranched polymers have been the focus of much research and development activity by both industry and academia over the past several years.[1,2] DSM has reported on the use hyperbranched polyester-amides in imaging applications.[3,4]

## Hyperbranched Acrylate Oligomers

Acrylates based on dendritic or hyperbranched molecules offer the potential to meet the conflicting demands of UV curable ink jet printing. In particular the compact more-or-less spherical shape results in a lack of chain entanglements and low hydrodynamic volume leading to low viscosity while the high concentration of acrylate groups provides attractive physical properties.

| Hyperbranched Acrylate Feature | Resulting Final Property |
|---|---|
| Spherical Shape | Low Viscosity<br>Low Shrinkage<br>Jetability |
| High Functionality | High Reactivity<br>Fast Cure<br>Hardness<br>Scratch Resistance<br>Chemical Resistance |
| High Molecular Weight | Water Resistance<br>Pigment Dispersion |

Hyperbranched acrylate oligomers can be made from hydroxy functional hyperbranched polyols by any of a variety of methods suitable for making acrylate esters including transesterification, direct esterification or reaction with acryloyl halides.

Sartomer Company has prepared acrylates of commercially available hyperbranched polyester polyols containing sixteen hydroxy end groups using standard acrylation methods. The extent of end group conversion to acrylates can be easily varied over a wide range, but to get the maximum advantage of the hyperbranched structure the conversion should be as high as possible. Molecular weight data for a product with approximately fourteen acrylate groups per molecule is shown in Table 1. Higher molecular weight/higher functionality products can also be made.

**Table 1. GPC Data.**

| | $M_n$ | $M_w$ | $M_p$ | $M_w/M_n$ |
|---|---|---|---|---|
| Hyperbranched Polyester Acrylate | 2200 | 2900 | 2400 | 1.32 |

**Table 2. Viscosity of Hyperbranched Polyester Acrylate vs. Conventional Acrylate Oligomers in Monomer Blends.**

| | # of Acrylate Groups | Functional Group Equivalent Weight | Viscosity in 50% 2PONPGDA @ Temp. |
|---|---|---|---|
| Hyperbranched Polyester Acrylate | 14 | 157 | 200 @ 25°C |
| Conventional Polyester Acrylate | 2 | 1300 | 1500 @ 75°C |
| Urethane Acrylate | 3 | 375 | 10,000 @ 25°C |
| Epoxy Acrylate | 2 | 250 | 1500 @ 25°C |

For ease of handling the hyperbranched acrylates are blended with multifunctional acrylate monomers. Table 2 shows how the viscosity of the hyperbranched polyester acrylate blended with an acrylate monomer – propoxylated neopentyl glycol diacrylate (2PONPGDA)[5a] - compared to viscosities of conventional radiation curable oligomers blended with the same monomer. The effect of the compact structure of the hyperbranched acrylate on blend viscosity is clear.

The speed at which UV cured ink jet printing can currently be done is limited by the cure speed of the inks being used. There is a need for raw materials that can boost the maximum cure speed of ink formulations to the limit attainable by current equipment designs. The rate at which acrylate monomers and oligomers cure depends mainly on functionality. The high concentration of reactive end groups in hyperbranched acrylate oligomers makes them effective cure-speed enhancers. The effect is especially evident in formulations containing low viscosity, relatively slow curing mono- and di-functional monomers. Table 3 shows a comparison of the maximum surface cure speeds of blends of a hyperbranched polyester acrylate oligomer vs. an epoxy acrylate oligomer at 50% concentration in low functionality monomers. Epoxy acrylates are generally considered to have good cure speeds, but use of the hyperbranched acrylates increases cure speed by 50% or more.

It should be noted that these blends are not optimized for cure speed. Inclusion of other monomers and appropriate photoinitiator choices should allow even faster cure rates.

As expected cured films prepared from hyperbranched polyester acrylate/monomer blends show excellent physical properties including hardness, strength, flexibility, abrasion resistance and chemical resistance. More surprisingly the films show relatively low shrinkage upon cure. Low shrinkage upon cure is usually associated with low functionality/high molecular weight materials. Higher functionality typically results in higher shrinkage. Low shrinkage upon cure is a desirable property as it often can be correlated with good adhesion to substrates. As shown in Table 4 the shrinkage of hyperbranched polyester acrylate/ monomer blends is actually lower than that of the low functionality monomers used in the blends.

**Table 3. Cure Speed of Hyperbranched Polyester Acrylate/Monomer Blends at 50 wt% Concentration.**

| Oligomer | Monomer | Monomer Functionality | Maximum Surface Cure Speed |
|---|---|---|---|
| Hyper-branched Polyester Acrylate | 2PONPGDA | 2 | 60 ft/min |
| Hyper-branched Polyester Acrylate | 3EO Phenol Acrylate[6] | 1 | 210 ft/min |
| Epoxy Acrylate | 2PONPGDA | 2 | 40 ft/min |
| Epoxy Acrylate | 3EO Phenol Acrylate | 1 | 120 ft/min |

**Table 4. Shrinkage Upon Cure of Hyperbranched Polyester Acrylates vs. Lower Functionality Monomers.**

| | % Shrinkage |
|---|---|
| Hyperbranched Polyester Acrylate Blended 50% in 2PONPGDA | 9 |
| 100% 2PONPGDA | 11 |
| Hyperbranched Polyester Acrylate Blended 50% in 3EOTMPTA[7] | 8 |
| 100% 3EOTMPTA | 11.5 |

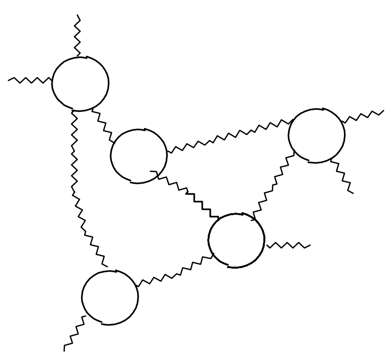

*Figure 2. Structure of Cured Films.*

In addition the cured films exhibit two distinct glass transitions by DSC and DMA analyses. The low shrinkage and the thermal measurements are both indicative of a two phase structure in which localized domains of high crosslink density are linked by less tightly crosslinked areas (Fig. 2).

## Conclusions

Dendritic or hyperbranched acrylates offer many attractive attributes as raw materials for UV cured ink jet printing. Among these are low viscosity, fast cure speed, low shrinkage and good cured physical properties.

Sartomer Company has recently introduced the first commercially available hyperbranched acrylate oligomers. Based on hyperbranched aliphatic polyester polyols the first two members of this new product family are available under the codes CN2300 and CN2301. Work is continuing to expand this new product line and explore the uses of hyperbranched materials in UV curing applications.

## References


1. G. R. Newkome, C. N. Moorefield, F. Vogtle, eds., *Dendrimers and Dendrons*, Wiley-VCH, 2001. G. R. Newkome, C. N. Moorefield, F. Vogtle, eds., *Dendritic Molecules*, VCH, 1996.
2. N. Rehnberg, B. Pettersson, U. Annby, M. Malmberg, US Patent 6,211,329 (2001), Perstorp AB. K. Sorenson, B. Pettersson, L. Boogh, J. Manson, US Patent 6,093,777 (2000), Perstorp AB.
3. A. Mukherjee, P. E. Froehling, "Hyperbranched Polyesteramides for Imaging Applications" *IS&T NIP 17 Proceedings*, pg 382.
4. P. E. Froehling, *Dyes and Pigments*, **48**, 187 (2001).
5. 2PONPGDA is available from Sartomer Company as SR9003.
6. 3EO Phenol acrylate is available from Sartomer Company as CD9087.
7. 3EOTMPTA is available from Sartomer Company as SR454.


## Biography

Jeffrey Klang has a BS in Chemistry from the University of Minnesota and a Ph.D. in Organic Chemistry from Cornell University. Since 1998 he has been with Sartomer Company as Manager, Monomer Development focussing on the design and production of novel UV curable acrylate monomers and oligomers.