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# Unique Characteristics of a Dendritic Polyether for Radiation Curing

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## Abstract

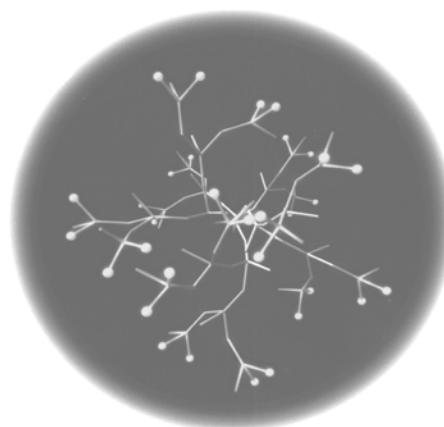
The combination of a high molecular weight, a high functionality and a low viscosity has always been a difficult issue to achieve with conventional oligomers in radiation curing. The benefits of a high molecular weight and high functionality would be numerous (increased physical reactivity, chemical resistance, toughness, low extractables, low shrinkage...) but this is hardly achievable with conventional polymer technologies when a very low viscosity is required like in radiation curing.

One of the major advances in polymer chemistry for the past 20 years has been the development of the so-called dendritic polymers. They consist of a more or less globular and high functional macromolecule without entanglements resulting in a lower viscosity than their linear or partly branched counterparts at a given molecular weight. Perstorp AB has developed a series of hydroxyl functional hyperbranched polyester based on dimethylolpropionic acid for the past 10 years and we recently developed a new dendritic polymer backbone, a polyether based on trimethylolpropane as the branching unit. In this paper, we present this new hydroxyl functional dendritic polyether and its potential application in radiation curing.

Two acrylated dendritic polyethers were synthesised and the UV cured coating properties were characterised. These polymers gave a unique combination of molecular weight (4000g/mol and 8000g/mol) and high functionality (16 and 32 acrylate functionality) while maintaining a very low viscosity (from 1.2 to 5.0 Pas at room temperature). This unique combination provides a large improvement in reactivity, chemical resistance and adhesion on difficult substrates compared to monomers based on a similar chemical structure, i.e. trimethylolpropane based monomers.

## 1. Introduction

Since the first synthesis of a dendritic polymer in the late 70's, growing interests for this new family of polymers have always extended for their unique and specific properties compared to their conventional linear and branched homologues (see Hult<sup>1</sup> and Fréchet<sup>2</sup> for a review). They are obtained by reacting a polyfunctional core with AB<sub>x</sub> monomers, typically AB<sub>2</sub> monomers, yielding to a "tree-like" amorphous structure (dendron means tree in ancient Greek). The obtained macromolecule is thus characterised by an exponential growth in both molecular weight and end group functionality.



**Figure 1.** Schematic illustration of a dendritic polymer

Dendritic polymers have traditionally been classified into 2 categories: dendrimers and hyperbranched polymers. A dendrimer is characterised by a perfect symmetrical globular shape which results from a step-wise controlled process giving a monodisperse molecular weight distribution. The second category, the hyperbranched polymer is attractive because they resemble dendrimers (their difference lies in their polydispersity and the less perfect globular shape) but they can be produced more easily on a larger scale and at a reasonable cost thus making them commercially available in large quantities today.

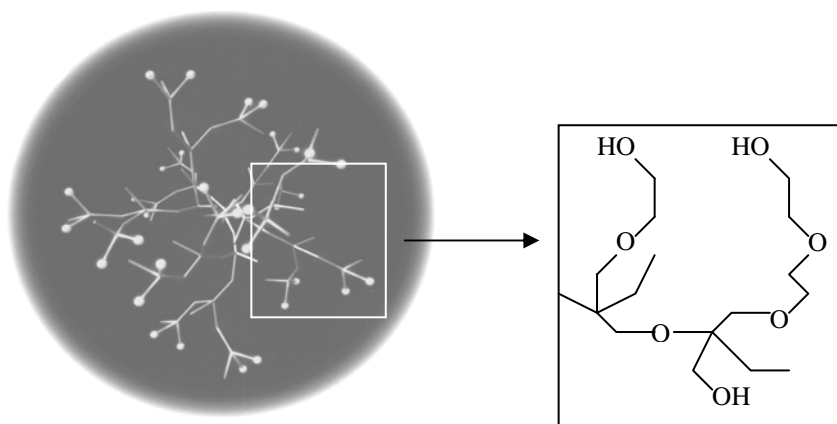
Unlike conventional polymers, the high number of end groups and their nature participate actively in the physical properties (solubility, glass transition temperature and viscosity) in combination with the backbone structure. This characteristic is exceptional since it leads to the possibility of designing the macromolecule with the combination of many different end groups nature, thus defining the type of reactive chemistry, properties and applications. The lack of entanglement results in a Newtonian behaviour with lower viscosity than the linear homologues (i.e. same nature and molecular weight). The solution viscosity is furthermore only slightly dependent on the molecular weight<sup>3</sup>.

The potential application in radiation curing and the benefits on reactivity, chemical resistance, mechanical properties and shrinkage of the dendritic polymers has been already highlighted based on a polyester backbone made from dimethylolpropionic acid in several papers<sup>4,5</sup>. Here is presented a new dendritic backbone based on trimethylolpropane (TMP) as the repeating unit, thus resulting in a polyether dendritic structure.

## 2. The dendritic polyether used in this study

### 2.1 Hydroxyl functional dendritic polyether

The hydroxyl functional dendritic polyethers are synthesised by ring opening polymerisation leading to a hyperbranched structure<sup>6,7</sup>. They consist of a polyalcohol as a core and trimethylolpropane units as chain extender, further extended by alkoxylation.



**Figure 2.** Representation of the dendritic polyether used in this study

Two hydroxyl functional dendritic polyether of different functionality were synthesised in order to obtain a theoretical molecular weight of approximately 3150g/mol and 6430g/mol with 16 and 32 hydroxyl groups respectively. Typical characteristics are given in the following table.

**Table 1.** Characteristics of the hydroxyl functional dendritic polyether used in this study

|                          | Mw<br>nominal<br>(g/mol) | Mn <sup>1</sup><br>(SEC)<br>(g/mol) | Mw <sup>1</sup><br>(SEC)<br>(g/mol) | OH number<br>(mgKOH/g) |      | Hydroxyl<br>functionality,<br>eq | Viscosity<br>(Pa.s, 30s <sup>-1</sup> , 25°C) |
|--------------------------|--------------------------|-------------------------------------|-------------------------------------|------------------------|------|----------------------------------|---|
|                          |                          |                                     |                                     | Nominal                | Exp. |                                  |   |
| Dendritic<br>Polyether 1 | 3150                     | 2033                                | 2575                                | 291                    | 286  | 16                               | 10  |
| Dendritic<br>Polyether 2 | 6430                     | 2690                                | 5204                                | 289                    | 281  | 32                               | 24  |

1. Determined by Size Exclusion Chromatography, Analytical Method PO-137-1, Perstorp Specialty Chemicals AB

These hydroxyl functional dendritic polyethers are low viscous liquids at room temperature.

## 2.2 Acrylation of the hydroxyl functional dendritic polyether and typical properties

The acrylated model compounds discussed later were based on the acrylation of the dendritic polymers described in the table 1. The acrylation of the products were made in a similar manner as for the acrylation of other polyether polyols. The dendritic polyether was charged together with acrylic acid (often in excess) together with an inhibitor, a Broenstedt acid and a solvent for azeotropic removal of water formed during reaction. When esterification was completed, the excess of acrylic acid removed by washing, precipitation etc. and the residual solvent was also removed. The resulting compounds were clear low viscous liquids at room temperature and they had the following characteristics:

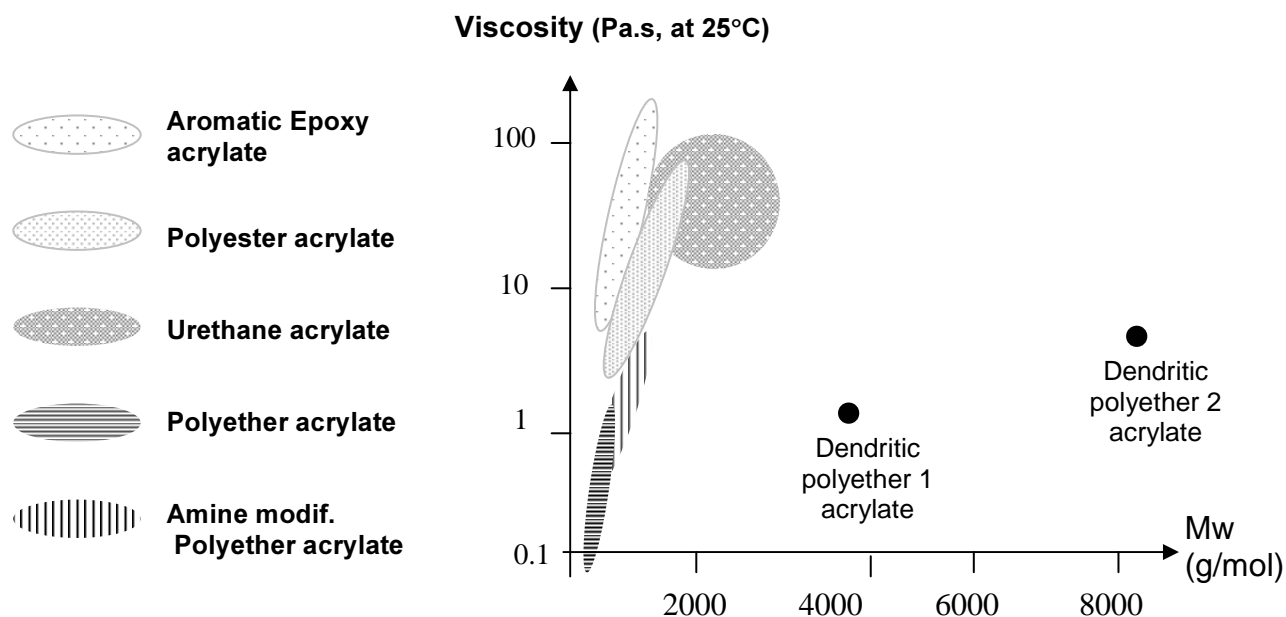
**Table 2.** Characteristics of the acrylate functional dendritic polyether used in this study

|                                      | Mw<br>nominal<br>(g/mol) | Mn<br>(SEC)<br>(g/mol) | Mw<br>(SEC)<br>(g/mol) | Acrylate<br>concentration<br>(mmol/g) | Nominal acrylate<br>functionality | Viscosity<br>(Pa.s, 30s <sup>-1</sup> , 25°C) |
|--------------------------------------|--------------------------|------------------------|------------------------|---------------------------------------|-----------------------------------|---|
| Dendritic<br>polyether 1<br>acrylate | 4024                     | 2610                   | 4125                   | 3.1                                   | 16                                | 1.2   |
| Dendritic<br>polyether 2<br>acrylate | 8158                     | 3025                   | 7066                   | 3.1                                   | 32                                | 5.0   |

As shown in table 2, the obtained dendritic polyether acrylates gave an exceptionally high average molecular weight (above 4000g/mol) with a low viscosity (below 5 Pas at room temperature).

### 3. Comparison with conventional acrylate oligomers

A comparison in terms of molecular weight and viscosity of the obtained acrylate polymers is done with commercially available acrylate oligomers (data compiled from commercial products of different manufacturers).



**Figure 3.** Comparison of the molecular weight/viscosity relationship of commercial acrylate oligomers<sup>8</sup> and the dendritic polyether acrylate

It is clearly shown on figure 3 that the advantage of the dendritic structure of the polyether gives a higher molecular weight than all the commercial oligomers (from 2 to 10 times higher) *and* a much lower viscosity than the majority of them.

Furthermore, it must be pointed out than most of the commercial oligomers presented here are diluted using a thinner (typically TPGDA or HDDA) up to 30-35% weight content compared to the 100% dendritic polyether.

## 4. Coating characterisation and comparison with trimethylolpropane based monomers

### 4.1 Physical Reactivity

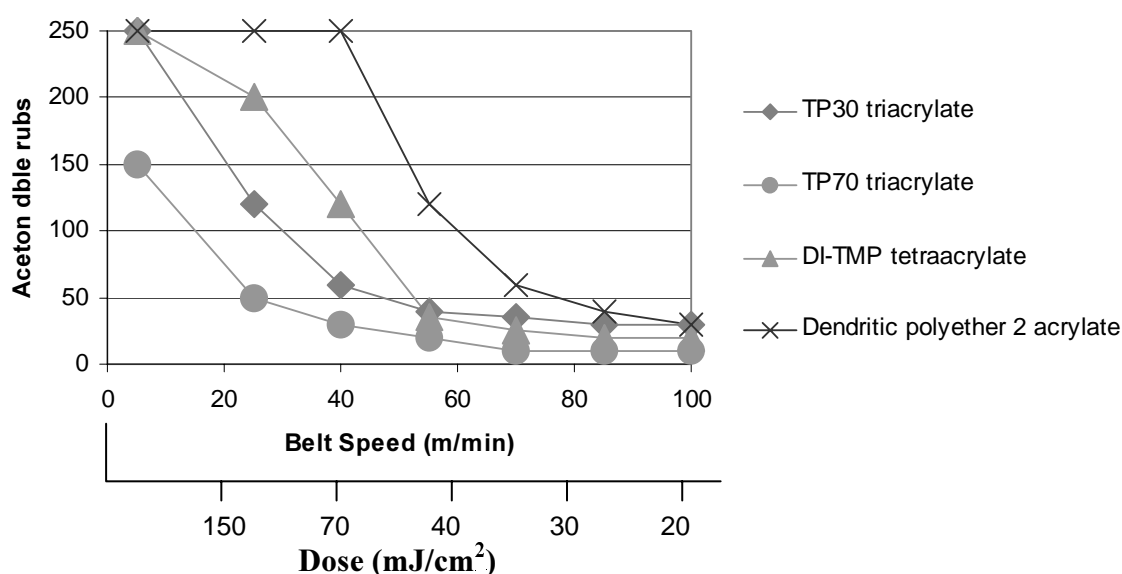
A comparison of the reactivity of some monomers based on trimethylolpropane and the dendritic polyether 2 acrylate was performed by measuring the acetone double rubs resistance (max. 250) of a 12 $\mu$ m thick coating cured on metal plates using 3% of Irgacure 500 (CIBA, Switzerland) after one pass under a UV source (lamp of 80W/cm) in air and by varying the belt speed (in other words by varying the UV dose).

The monomers based on trimethylolpropane (TMP) were polyols from Perstorp AB, Sweden. Ethoxylated trifunctional TMP with 3 and 7 ethylene oxide groups (TP30 and TP70 respectively) and the tetrafunctional Ditrimehylolpropane (DiTMP) were acrylated according to the same process as explained in section 2.2. The theoretical molecular weight, the acrylate concentration and the typical viscosity of the acrylates are given in the following table.

**Table 3.** Characteristics of the acrylate compounds used for comparison

|                                     | TP30A<br>Ethoxylated TMP<br>(3EO) triacrylate | TP70A<br>Ethoxylated TMP<br>(7EO) triacrylate | Di-TMPA<br>tetraacrylate | Dendritic<br>Polyether 2<br>acrylate |
|-------------------------------------|---|---|--------------------------|--------------------------------------|
| Mw (nominal)                        | 428   | 604   | 468                      | 8158                                 |
| Acrylate conc.<br>(nominal, mmol/g) | 7   | 4.9   | 8.5                      | 3.9                                  |
| Viscosity (Pas at 25°C)             | 0.1   | 0.1   | 1                        | 5                                    |

The comparison of the reactivity is given in figure 4.



**Figure 4.** Comparison of the reactivity of the dendritic polyether 2 acrylate with the model compounds

Even if the dendritic polyether had the lowest acrylate concentration (up to 2 times lower than Di-TMP tetraacrylate), the best reactivity was obtained by the dendritic polyether where above 250 acetone double rubs were still reached at a speed of 40m/min and relatively low dose (70mJ/cm<sup>2</sup>).

The starting high molecular weight of the dendritic polyether is believed to result in a faster growth rate of the microgels particles thus resulting in a very early gel point. The property built-up is then much faster than starting from low molecular weight monomers.

## 4.2 Hardness and flexibility of fully cured coating

Fully cured coating was ensured by allowing the coating samples containing 3% of Irgacure 500 to pass 4 times under a UV source of 240W/cm at 20m/min under air. The obtained film properties are reported in table 4.

**Table 4.** Coating properties of fully cured compounds

|                              | TP30A<br>Ethoxylated TMP<br>(3EO) triacrylate | TP70A<br>Ethoxylated TMP<br>(7EO) triacrylate | Di-TMPA<br>tetraacrylate | Dendritic<br>Polyether 2<br>acrylate |
|------------------------------|---|---|--------------------------|--------------------------------------|
| Hardness<br>[ks]             | 189   | 83  | 207                      | 119                                  |
| Erichsen Flexibility<br>[mm] | 2.4   | 4   | <1                       | 3.7                                  |

Due to its high acrylate concentration, Di-TMPA gave a very hard and scratch resistant film but to the detriment of the flexibility.

The high molecular weight of the TMP based dendritic polyether and its combination of the flexible backbone and branched structure result in a tough coating with medium hardness *and* flexibility compared to the TMP based monomers. Compared to TP70A, almost the same flexibility was reached but a significantly higher hardness was obtained.

## 4.3 Chemical resistance

The coatings cured in section 4.2 were exposed to acetone for 5 minutes and 1 hours. The results are shown in table 5.

**Table 5.** Acetone resistance of the dendritic polyether and the comparison with the TMP based monomers

|               | TP30A<br>Ethoxylated TMP<br>(3EO) triacrylate | TP70A<br>Ethoxylated TMP<br>(7EO) triacrylate | Di-TMPA<br>tetraacrylate | Dendritic<br>Polyether 2<br>acrylate |
|---------------|---|---|--------------------------|--------------------------------------|
| Acetone 5 min | OK  | complete lifting                              | OK                       | OK                                   |
| Acetone 1 hr  | OK  | -   | OK                       | OK                                   |

No effects were observed after 1 hour of exposure in the case of the dendritic polyether despite its much lower acrylate concentration than all the TMP based monomers. It is even better than the highly ethoxylated TP70 triacrylate where complete lifting is observed after approximately 5 minutes of exposure.

## 5. Adhesion on polyethylene

The main parameters affecting the adherence of UV cured coatings on non porous and non swellable substrates like polyolefins are<sup>9</sup>:

- the wetting of the substrate
- the glass transition temperature of the coating and the shrinkage
- the coating network and its molecular weight

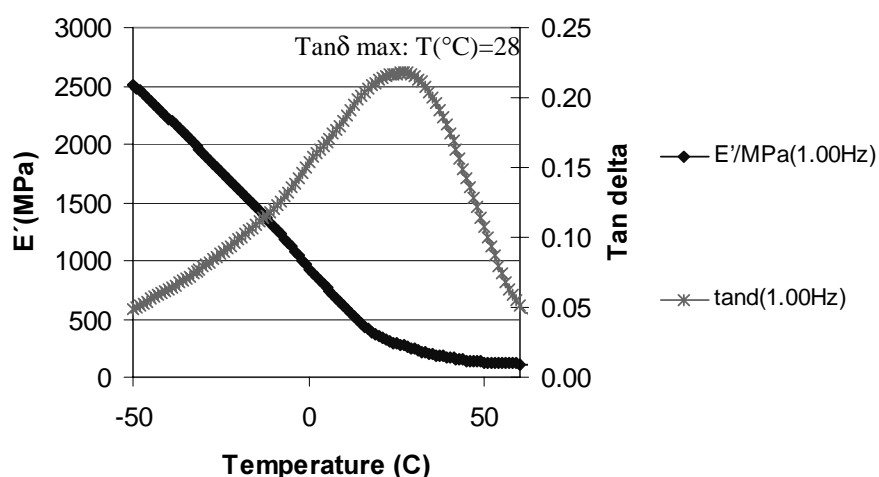
A good wetting is achieved with two conditions:

- the surface tension of the liquid needs to be equal or lower than the surface tension of the solid
- a low viscosity contributes to improved wetting

Low glass transitions together with a low shrinkage are essentials to achieve good adherence. A high glass transition (above room temperature) with a high shrinkage would lead to high residual stresses after curing and this could initiate debonding between the coating and the substrate.

As already reported in radiation curing technology<sup>10</sup>, high molecular weight hyperbranched polymers yield to a low shrinkage which is believed to be true in the case of the new dendritic polyethers presented here.

Furthermore, a cured film from the dendritic polyether 2 acrylate has an excellent hardness to flexibility ratio which is explained by its relatively low glass transition temperature (28°C, taken from Tan  $\delta$  max, 1 Hz, of a DMA measurement performed on a fully cured film in a tension mode - instrument: Netzsch 242). The DMA measurement is shown on figure 5.



**Figure 5.** Tension mode DMA measurement ( $E'$  and  $\text{Tan } \delta$ ) of a fully cured dendritic polyether 2 acrylate film (0.04\*10\*8mm) with 3% Irgacure 500 cured after 4 passes under a 240W/cm Hg lamp under air

Finally, the dendritic polyether 2 acrylate has a unique high molecular weight (8000g/ mol) with a low viscosity (5 Pas@25°C).

These elements make the dendritic polyether acrylate an ideal oligomer for providing a good adherence on difficult substrate.

In order to evaluate the adherence on a difficult substrate, the cross hatch test was performed on 12µm thick coating cured on polyethylene (corona treated) with 3% Irgacure 500 after 4 passes under a 240W/cm lamp in air. The dendritic polyether 2 acrylate and the TMP based monomers presented in the section 4 were tested as well as a simple formulation consisting of 50 parts of the dendritic polyether 2 and 50 parts of TP30 triacrylate. It can be noticed that this formulation has a viscosity of 550mPas at 25°C (measure by a cone and plate rheometer) without the use of irritating monomers like TPGDA or HDDA. The results are presented in table 6.

**Table 6.** Comparison of the cross hatch test on fully cured coatings (0-5; 0:best, no effects)

|  | TP30A<br>Ethoxylated TMP<br>(3EO) triacrylate | TP70A<br>Ethoxylated TMP<br>(7EO) triacrylate | Di-TMPA<br>tetraacrylate | Dendritic<br>Polyether 2<br>acrylate | Dendritic<br>Polyether 2<br>acrylate<br>+<br>TP30A<br>(50:50) |
|--|---|---|--------------------------|--------------------------------------|---|
| Cross hatch<br>test on PE<br>(cross-cut)<br>(0-5, 0 best,<br>no effects) | 4   | 5   | 3                        | 0                                    | 0   |

The best results are obtained with the dendritic polyether as 100% as well as the formulation containing the TP30 triacrylate where the coating stayed unaffected by the test. It can be noticed that TP30 triacrylate as 100% does not give a good adhesion on this substrate (rated 4).

## 6. Conclusions

A new dendritic polymer based on trimethylolpropane as the branching unit was presented. The dendritic structure is a hydroxyl functional polyether which allows acrylation for application in radiation curing. The acrylated dendritic polyether had for principle features to yield extremely high molecular weight (8000 g/mol, i.e. up to 10 times higher than conventional oligomers) with a lower viscosity than most of the commercial oligomers (less than 5 Pas at room temperature has been obtained with the dendritic polymers).

Together with its high functionality (32 acrylate groups), this unique combination of properties gives coatings with very high physical reactivity thanks to the very fast properties built-up upon photopolymerisation.

The alternance of flexible segment (ether linkage) and the hyperbranched structure allows a very good compromise between hardness and flexibility, resulting in a tough coating. The chemical resistance is as well very good compared to some alkoxyated TMP based monomers.

Finally, the relatively low glass transition temperature, the good wetting properties as well as the high molecular weight and the low shrinkage result in a very good adhesion for difficult substrate such as polyolefins. Thanks to its inherent low viscosity, it is possible to obtain a low viscous formulation with a limited amount of reactive monomers and/or avoiding the use of some irritating low viscous diluents.

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