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Performances of an acrylated dendritic polyester in a UV coating formulation

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Summary

Dendritic polymers are a new class of polymer, characterised by a densely branched backbone and a large number of reactive groups. 2 main characteristics of such a structure is the lack of entanglements and the low hydrodynamic volume resulting in a lower viscosity than linear or branched analogues. Dendritic polymers have already shown specific properties enhancements in a wide range of applications (as processing aid, toughening agent, and promoting agent). New application areas are still discovered, showing the high potential of such a technology.

In Rad-cure applications, trends towards highly reactive formulation allowing higher productivity and/or lower photo-initiator level (printing inks) are becoming more and more stringent. The high molecular weight, the high crosslinking density and the high number of functionality combined with a low viscosity compared to conventional system seem to be a valuable solution to achieve these goals.

The high reactivity of using dendritic polyester acrylates (curing without photoinitiator is possible in air and with a low lamp intensity) has already been reported¹. Here are presented the performances of a 16 acrylate functionality aliphatic polyester dendritic oligomer (Mw=2600g/mol) in a UV formulation. High reactivity, deep and homogenous curing depth, low curl, high chemical resistance, better scratch resistance and low extractables are some of the multiple advantages of using dendritic polyester in a UV formulation.

This new kind of oligomer is an opportunity to open and extend new applications for Rad-cure technology as for example food packaging printing inks (low photo-initiator concentration as well as low extractable) or electronic applications (deep and homogenous curing depth).

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 Hult² and Fréchet³ for a review). They are obtained by reacting a polyfunctional core with AB_x monomers, typically AB₂ 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.

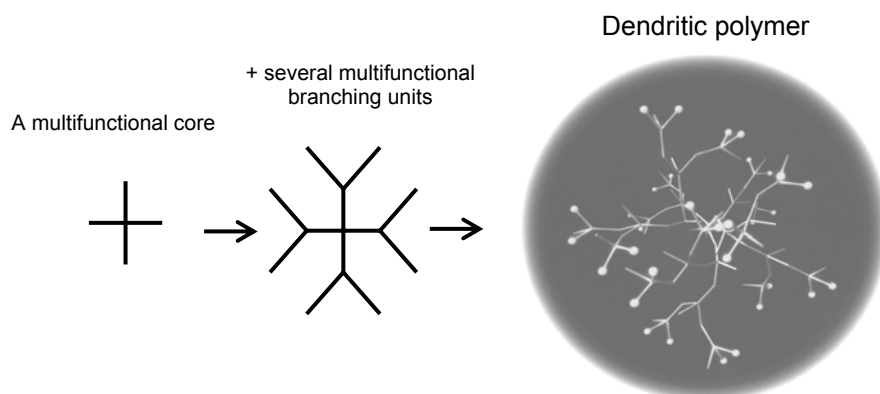


Figure 1. Schematic growth synthesis and illustration of a dendritic polymer

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.

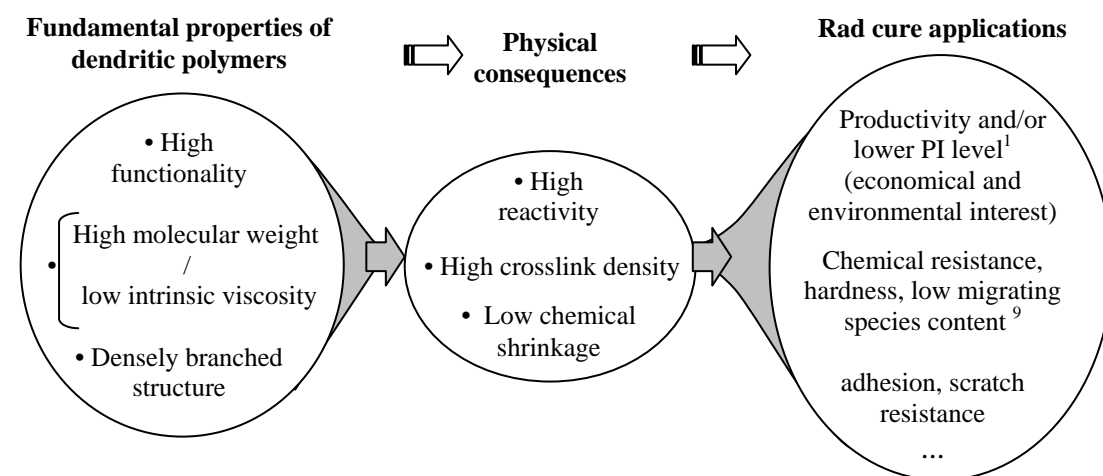
Unlike conventional polymer, the high number of end groups and their nature participate actively in the physical properties (solubility, glass transition temperature and viscosity) in combination with the backbone structure. This characteristic is exceptional since it leads to the possibility of designing 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 weight⁴.

The applications are numerous and some important fields of the presented dendritic polymers in the plastic industry can be mentioned as:

- polymers additives (processing aids, compatibilizers for thermoplastics and toughener agents for thermosets⁵)
- polymer building blocks for coatings^{6,7,8} (alkyds, powder coatings and radiation curable coatings)

2. Dendritic polymers for Rad-cure technology

Radiation-curable technology is an ideal application to explore all the potential of such a macromolecule used as a building block. The combination of its characteristics makes the dendritic polymer a unique and promising candidate to today's stringent coatings quality requirements. The fundamental specific properties of dendritic polymers and their potential impact on coating performances can be summarised as following:



Furthermore, the versatility of the technology (the type of core, the nature of the backbone, the number of generation and the shell structure) provides a wide range of different properties (viscosity, reactivity and flexibility/hardness). An appropriate design can lead to specific desired properties for any particular applications.

3. Dendritic Polymer in this study

The starting dendritic polymer used in this study is an aliphatic hydroxyl functional polyester^{10,11}. This is a hyperbranched polymer polyol commercially available today in large quantities¹². Different grades of these dendritic polyols cover a wide range of molecular weight (from 1750g/mol to 7500g/mol). They are amorphous solids with glass transition temperatures from 30 to 40°C. The dendritic polyester type is shown on figure 2.

Product property ¹³	Typical value
Molecular weight-nominal, g/mole	1750
Hydroxyl functionality-nominal, eq	16
Molecular weight (SEC), Mw, g/mol	2100
Molecular weight (SEC), Mn, g/mole	1600
Polydispersity index, Mw/Mn	1.3
OH-value, nominal, mg KOH/g	513
OH-value, typical, mg KOH/g	509
Acid value, typical, mg KOH/g	6
Density, g/cm ³	1.295
Tg (DMTA), tan δ max, °C	30
Viscosity , 110°C, 30 s-1, Pas	5

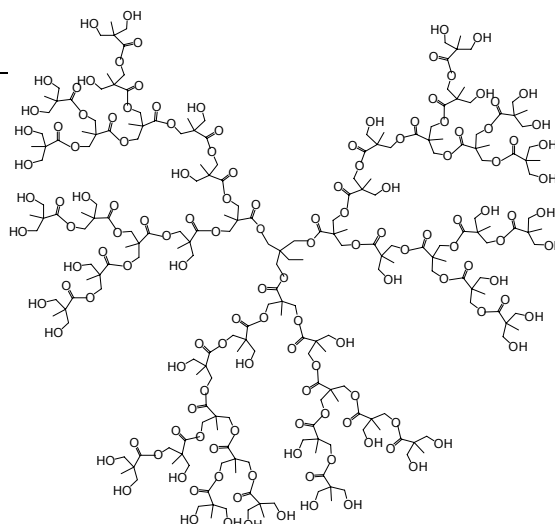


Figure 2. Properties of the starting dendritic polyester polyol and illustration

The acrylated model compounds discussed later are based on acrylation of the dendritic polymer described in the table of figure 2. Acrylation of the product is made in similar manner as for acrylation of other polyester acrylates. The dendritic polyester is charged together with acrylic acid (often in excess) together with an inhibitor, a Brønsted acid and a solvent for azeotropic removal of water formed during reaction. When esterification is completed, the excess of acrylic acid removed by washing, precipitation etc. and the residual solvent is also removed.

Obtained product is a yellow transparent liquid at room temperature and it has the following properties:

Molecular weight	Acrylate functionality	Acrylate concentration	Viscosity
Mw, g/mole		(mmol/g)	(Pa.s, 23 °C)
2614	16	6.12	180

Table 1. Properties of the acrylated dendritic polyester used in this study

4. Properties of the neat acrylated dendritic polyester

The viscosity of the dendritic polyester was evaluated at 23°C and a comparison with conventional oligomers¹⁴ is presented on figure 3 as a function of the molecular weight.

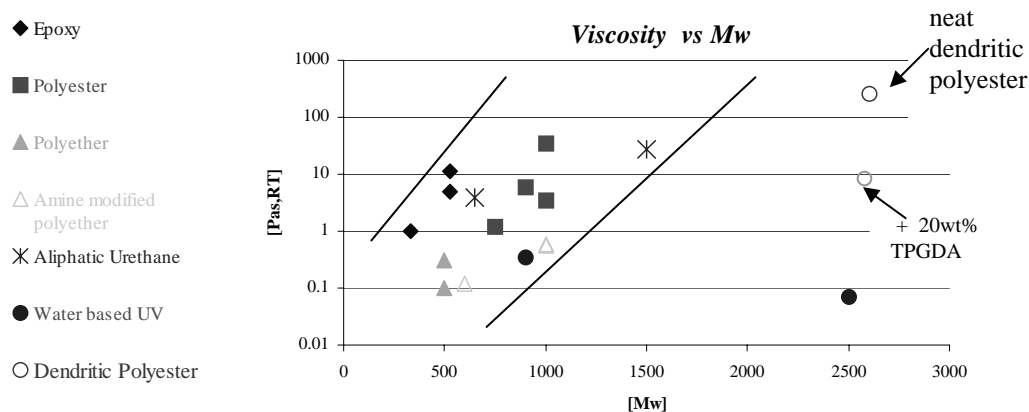


Figure 3. Viscosity as a function of Molecular weight

Epoxy acrylates have the highest ratio viscosity/molecular weight together with polyurethane acrylates and polyester acrylates and then polyether acrylates. Water based UV oligomers (emulsion and dispersion) are specific to this respect since viscosity is independent of molecular weight. The dendritic characteristic of the hyperbranched polyesters resulting in a low hydrodynamic radius and no entanglements is clearly shown on this picture, i.e. low viscosity for high molecular weight can be achieved. These products do not behave as conventional polyester acrylates.

It can be mentioned that the conventional oligomers presented here with a viscosity higher than 10 Pa.s are diluted using a thinner (HDDA, TPGDA) in concentration from 15wt% to 35wt%. As indicated, adding 20wt% of TPGDA (viscosity around 12 mPa.s at room temperature and Mw=300g/mol) reduces the viscosity of the dendritic polyesters below 10 Pa.s, thus a similar and even lower viscosity than the other diluted oligomers (polyester, epoxy or polyurethane).

From 2 to 6 times higher molecular weight than conventional polyurethanes, polyesters and epoxies respectively for a similar viscosity is obtained. Compared in general to other families of conventional acrylated oligomers (except water based systems), this is the only one to achieve as high molecular weight (>2600 g/mol) for such low viscosity.

The neat dendritic polyester acrylate was cured in similar conditions as the oligomers presented in reference 15. Film of 50µm cured with 4% Irgacure 500 and a total dose of 1300 mJ/cm² under a mercury UV lamp of 80W/cm). The coatings properties were evaluated in terms of surface conversion by Attenuated Total Reflectance FTIR (Nicolet Protégé 460 by monitoring the decrease in vinyl groups absorption at 810cm⁻¹ and by normalisation with the carbonyl absorption peak at 1740cm⁻¹. Correlation with pendulum hardness (König, second) is illustrated on figure 4.

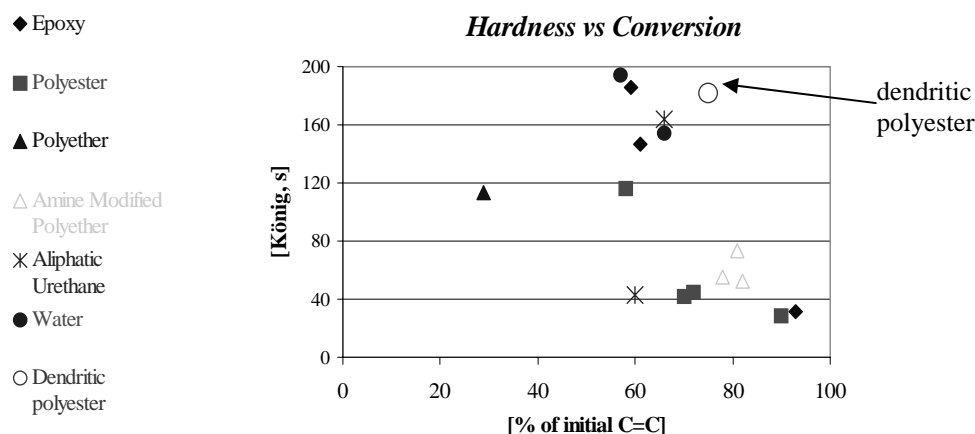


Figure 4. Hardness as a function of surface conversion

Amine modified polyethers and polyesters have usually medium hardness and medium glass transition temperature (from -3°C to 60°C). The low glass transition temperature around processing temperature (slightly above room temperature due to the exothermic reaction) allows a high ultimate conversion since vitrification (when a slow diffusion controlled polymerisation rate starts) is not reached or at least only at a high conversion.

Although the dendritic polyester acrylates have a high number of functionality, a conversion similar to conventional oligomers of lower functionality is obtained. The high functionality results in a hard film with high glass transition temperature similar to aromatic epoxies (hardness around 180 Ks and Tg around 90 degrees). Due to the aliphatic backbone of the dendritic polyester, a better flexibility compared to aromatic epoxies is expected. In combination with the easy accessibility of the acrylate groups on the shell structure, it can explain the excellent conversion (78%) for a high Tg obtained with curing at room temperature (the Tg is 90°C from Tanδ obtained by Dynamic Mechanical Analysis, result not shown in this paper).

5. Formulation example using the dendritic polyester

Materials

The reference formulation consists of an amine-modified polyether (40part) and a reactive diluent (60parts), an alkoxyated pentaerythritol (PEOTA), which both are known to be highly reactive and give good chemical resistance. The blend has a viscosity of 600 mPa.s at 23°C as measured by a plate and plate Stress-Tech viscometer (in a constant shear rate mode).

Component	Viscosity (mPas) at 23°C	Acrylate Functionality	Mw (g/mol)
H2O A	180 000	16	2 614
PEOTA	160	4	-
Amine modified polyether	3 000	4	1 000

Table 2. Properties of the components used in the formulations

The dendritic polyester formulation consists in 20 part of the dendritic polyester, 20 parts of the amine modified polyether and 60 parts of the diluting monomer. The viscosity is 1000 mPa.s as measured in the same conditions than the reference.

Shrinkage and Modulus of the components

Shrinkage and modulus were measured in a photo-rheometer (rheometric science ARES LS) using a spot cure lamp (EFOS Novacura UV light N2000 of 15mW/cm²). The shrinkage is the linear shrinkage obtained during curing. The modulus G' given on figure 5 is the ultimate modulus measured after long exposure time (120s) using 1% of Darocur 1173.

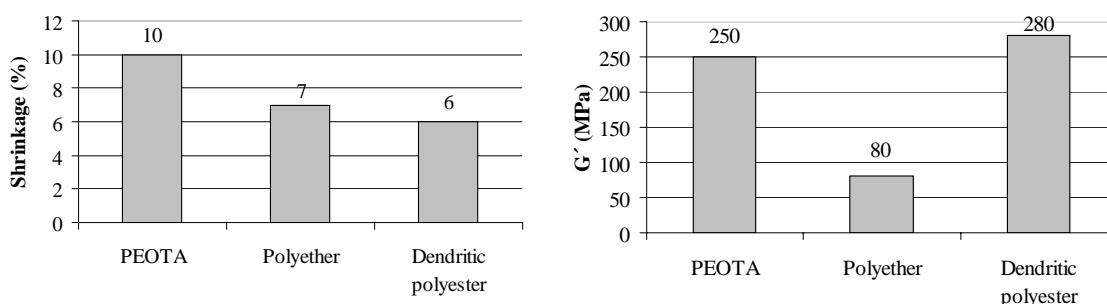


Figure 5. Shrinkage and G' modulus as measured by photo-rheometry

As expected the reactive diluent has the highest shrinkage (10%) and the dendritic polyester the lowest (6%) illustrated the effect of the densely branched structure. The amine modified has a very low modulus (80MPa) and is highly flexible. The dendritic polyester has the highest modulus due to the very high crosslinking density and its higher glass transition temperature compared to the 2 other constituents.

Hardness and chemical resistance as a function of photoinitiator level

Samples were cured at different photoinitiator level (2% and 0.25% of Darocur 1173) on metal plates. Thickness was 12 µm applied with a K-bar and the samples were cured at 40m/min under air with a medium pressure Hg lamp (80W/cm). Samples of 2, 4 and 8 passes under the UV source were generated. Samples were tested 24 hours after being manufactured.

As it can be seen on figure 6, an increase in hardness of about 50 Ks is observed for the dendritic polyester modified formulation as well as a significant increase in chemical resistance (>500 acetone rubs from 4 passes). Similar hardness is obtained for the dendritic polyester formulation using only 0.25% of PI as the reference cured with 2%PI (around 140Ks after 8 passes). Cured with 0.25%PI, the chemical resistance is still much higher than the reference material cured with 2%PI (respectively >500 acetone dbl. rubs and 250 after 8 passes). The latter has a very bad chemical resistance with 0.25% PI showing very poor cure.

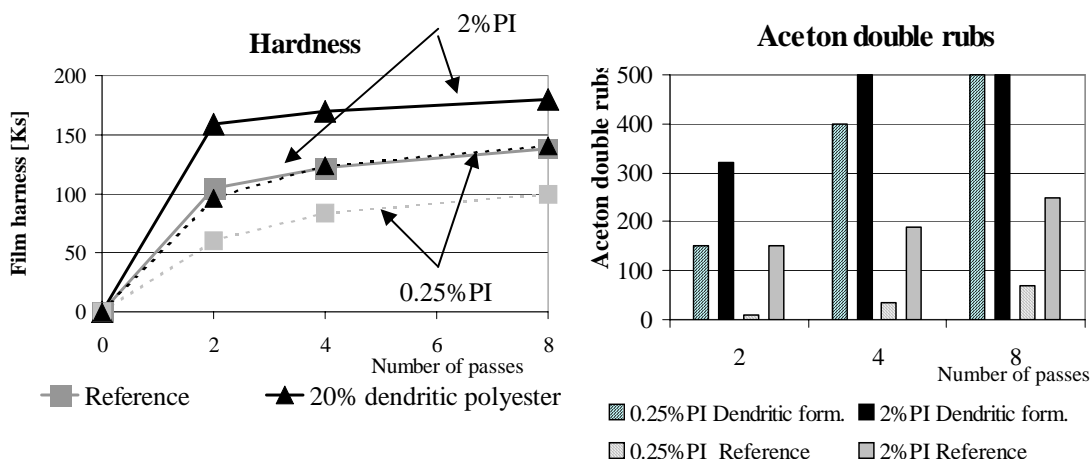


Figure 6. Hardness and acetone double rubs for 2 photoinitiator concentration (2wt% and 0.25% of Darocur 1173) as a function of the number of passes under the source

Extractable

The advantage of using a low photoinitiator content without altering the properties of the coating is obvious since it is believed that less fragments of photoinitiator will be present in the coating. Thermogravimetry (TGA1000, Polymer Lab with a temperature gradient of 10°C/min under nitrogen) has been performed on the samples taken from the coating cured after 8 passes in the conditions discussed in the preceding section. The samples are the ones giving similar properties, the reference with 2wt% PI and the dendritic modified formulation with 0.25wt % PI.

Weight loss	1%	2%	3%	5%	6%
Reference +2%PI	139	193	216	251	278
20wt% dendritic polyester +0.25% PI	150	256	298	328	358

Table 2. Temperature (°C) corresponding to a given weight loss

Darocur 1173 is known to be highly volatile and specially in a range 100-200°C. This is illustrated here since reducing the PI from 2wt% to 0.25wt% result in an increase of at least 60°C for similar loss in weight.

Curing depth

The resin was poured (with 2wt% Darocur 1173) in a small aluminium foil mould (diameter 25mm, height 5mm). The mould was exposed to the UV source (80W/mm, 20m/min in air) and the sample removed after 8 passes. The bottom side was not cured but the liquid resin was removed. Then using FT-IR and by cutting at different thickness the sample, conversion could be determined.

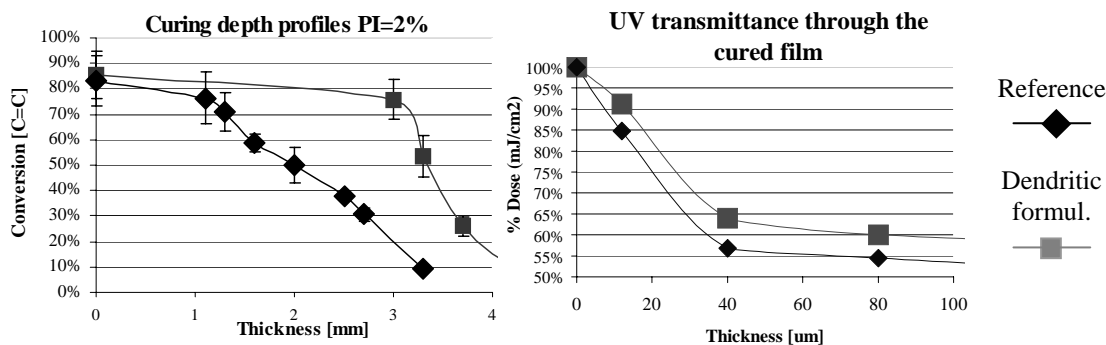


Figure 7. Curing depth profile and UV transmittance through cured films (% of the UV initial dose at a given thickness)

The main reason for a higher coating thickness (more than 3 times higher thickness for a conversion superior to 75%) is due to a lower UV absorbency of the cured polymer as shown on figure 7. This interesting property results in a more homogenous curing through the thickness (low gradient in conversion through the depth with number of passes). Together with the lower shrinkage of the dendritic polyester, this could be the main reason for less curl and better adhesion properties.

6. Conclusion

The fundamental properties of dendritic polymers have been demonstrated in rad-cure applications by using an aliphatic dendritic polyester. Thanks to the globular hyperbranched shape without entanglements, from 2 to 6 times higher molecular weight is obtained for a similar viscosity compared to conventional oligomers. The high crosslinking density leads to coatings of similar hardness as aromatic epoxies (above 180Ks) which is exceptional for an aliphatic structure. Furthermore the inherent backbone flexibility and easy accessibility of the acrylate groups allow to reach a high ultimate conversion (around 80% of the acrylate functions) in combination with a high glass transition temperature (90°C). Excellent chemical resistance is as well observed.

Adding the dendritic polyester in a highly reactive and chemical resistant formulation leads to improved reactivity and chemical resistance even at low concentration (20wt% of dendritic polyester). Lower PI level can then be used resulting in lower extractables. A lower shrinkage is as well observed and together with a homogenous and deeper through curing, this could contribute to improved adhesion.

The versatility in designing the hyperbranched polyester makes it as a unique tool for structure/properties relationship allowing to reach unique combinations of properties that are not possible with conventional oligomers.

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