Hyperbranched polymers for hardcoat with superior performances

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Abstract

Combining environmental and productivity benefits, UV/EB technology is attractive for hardcoat applications as high abrasion resistance can be achieved. Wood coatings, CD/DVD, LCD displays for mobile phones, touch panel displays, polycarbonate headlamp applications are examples where Radcure technology is well established. However, new applications like flexible displays, new generation of electronic storage devices or in-mould decoration also mean new requirements like improved dimensional stability, higher flexibility, lower viscosity and better adhesion.

In this paper, we present a new precursor for the preparation of acrylic esters based on hyperbranched aliphatic polymer polyols. The unique molecular structure of the hyperbranched polymers provides high functionality at low viscosity and allows further improvements in all above mentioned properties, compared to state of the art high functionality acrylates typically used in hardcoats like Di-Pentaerythritol hexaacrylate. A unique combination of properties like high hardness, scratch resistance and flexible hardcoats with low viscosity and low shrinkage can be achieved.

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[1] and Fréchet[2] for a review). They are obtained by reacting a poly-functional core with ABx 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.

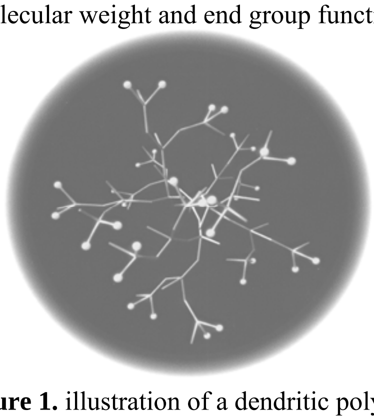

Figure 1. illustration of a dendritic polymer

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 weight[3].

The applications are numerous and some important fields polymers can be mentioned as:

- polymers additives (processing aids, compatibilizers for thermoplastics, toughener agents for thermosets[4] and polyurethane foams[5])
- polymer building blocks for coatings [6,7,8] (high solid alkyds, powder coatings and radiation curable coatings)

2. Dendritic polymers for radiation curing 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 in figure 1.

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.

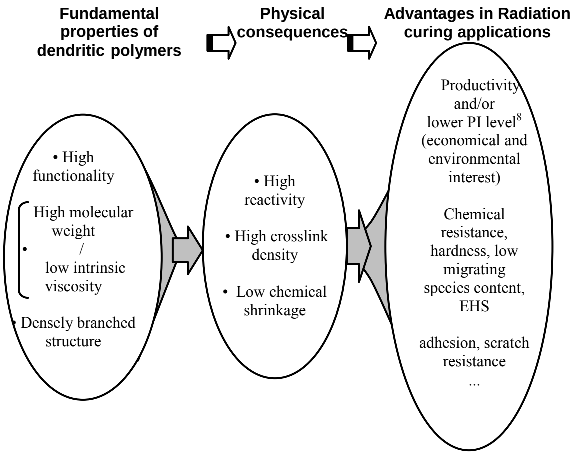

Figure 1. Major advantages of the dendritic polymers technology for UV/EB technology

A low viscous dendritic polymer has already been developed especially for radiation curing applications[10] exhibiting the mentioned performances like low viscosity at high molecular weight, high wear resistance and low extractables.

3. Properties of the hyperbranched polyol used in this study

The hyperbranched polymer used to prepare the acrylic ester in this paper is a new clear low viscous hydroxyl functional aliphatic hyperbranched polyester/ether blend having characteristics given in table 1.

Table 1. Characteristics of the hyperbranched polyol used in this study

	Molecular weight	OH number	Acid number	Viscosity
	Mw (SEC, g/mol)	mgKOH/g	mgKOH/g	Cone & plate (Pa.s, 25ºC, 30s^{-1})
Dendritic polyol[11]	**1600**	**590**	**max 3**	**14**

The characteristics of the acrylated hyperbranched polyol synthesized according to conventional esterification process with acrylic acid are presented in table 2. A simple comparison of viscosity as a function of molecular weight for 5 types of conventional oligomers used in radiation curing is given in figure 2.

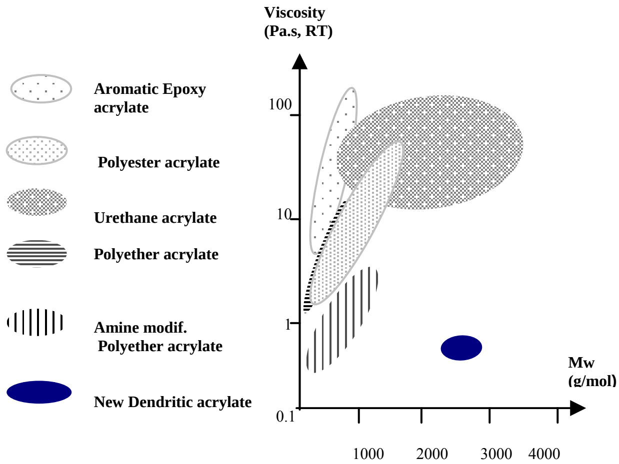

Figure 2. Comparison of molecular weight (Mw) and viscosity (Pa.s at room temperature) of conventional oligomers used in radiation curing

Table 2. Characteristics of a typical acrylated dendritic polyol

	Molecular weight	Acrylate conc.	Acid number	Non VOC	Density	Viscosity	Shrinkage	Refractive index	Tg (cured film)
	Mw (SEC, g/mol)	mmol/g	mgKOH/g	%	g/cm^3	Cone & plate (mPa.s,25°C, 30s^{-1})	%	22°C (cured film)	DMA, (Tan δ max)ºC
Typical values	**2700**	**5.5**	**2.0**	**>99**	**1.168**	**750**	**10**	**1.513**	**90**

4. Coating characterization

4.1 Basic comparison

The new dendritic acrylate was compared with two other high functionality acrylates, Di-Pentaerythritol penta/hexaacrylate (DPHA, acrylic ester of Di-Pentaerythritol, polyol obtained from Perstorp Specialty Chemicals AB, Sweden) and an ethoxylated pentaerythritol tetraacrylate (acrylic ester of PP50S, a tetrafunctional polyether poyol from Perstorp Specialty Chemicals AB, Sweden). All tests were done with 3% Irgacure 500 obtained from CIBA, Switzerland. The UV curing unit was a Fusion F600 equipped with one H bulb.

From table 3, the new dendritic acrylate exhibited the following characteristics:
- a significantly lower viscosity than DPHA
- as good surface cure as DPHA, better than PP50S
- as good flexibility as PP50S acrylate
- almost as good hardness as DPHA
- almost as good water and ethanol resistance as DPHA

4.2 Scrub scratch resistance

The scratch resistance was evaluated by Scotch-Brite (green) rubs (constant weight of 500gr) and by measuring gloss retention (20º and 85°) as a function of cycles (50, 100, 150 and 200 rubs) and a UV dose of 500 mJ/cm^2, 2 pass at 12 m/min for 40 µm thick films on black panels). The results are reported in figure 3.

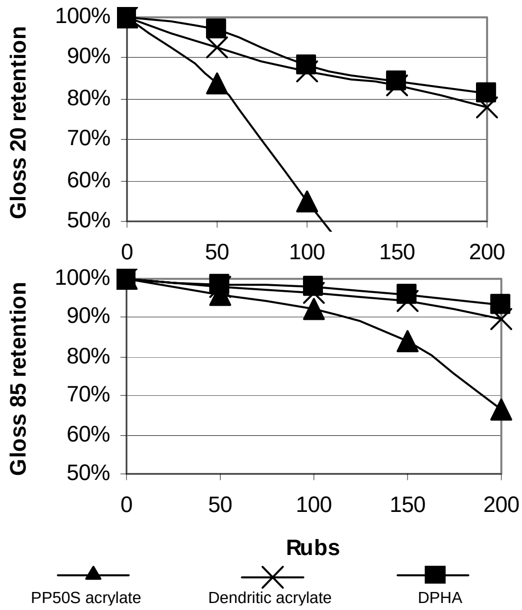

Figure 3. Gloss retention (20° and 85°) during scrub test for a UV dose of 500 mJ/cm^2

The new dendritic acrylate and DPHA demonstrated a very high scratch resistance as seen by gloss retention. It was significantly better than the tetrafunctional PP50S acrylate and similar to the DPHA.

Table 3. Basic comparison of UV cured films with a UV dose of 500 mJ/cm^2 (2 pass at 12 m/min under 160W/cm H bulb in air)

	DPHA	PP50S acrylate	New dendritic acrylate
Viscosity, mPas, Cone & plate 25 °C	14000	200	700
Minimum cure speed for tack free surface (m/min , 1p, 12 um on Al plates)	2*15	2*10	2*15
Corresponding UV dose (mJ/cm^2)	200	300	200
Pencil hardness (40µm on glass)	6H/7H	4H/5H	5H/6H
Pendulum hardness (40µm on glass), König.s	163	156	165
Erichsen flexibility (120W/cm, 12 µm on Al plates)	0,4	2,2	2,2
Water resistance 48 hrs (40 µm on glass plates) 0 to 5, 5 best	5	4	4
Water: ethanol (1:1) resistance 48 hrs (40 µm on glass plates) 0 to 5, 5 best	4	3	4

4.3 Hardcoats on polycarbonate (PC)

The influence of the substrate is important for pencil hardness, especially at low film thickness (as compared to hard substrates like glass). A basic comparison was performed on polycarbonate sheet (Lexan 8010C, 250µm, from GE) for the pure acrylates cured with 3% Irgacure 500 under a 160W/cm H bulb in air. The coatings were conditioned at 25°C and 50%RH for 24 hours before testing.

The new dendritic acrylate yielded similar pencil hardness as DPHA at high film thickness as shown in table 4. The new dendritic acrylate exhibited significantly better adhesion than DPHA on PC (see table 5) as well as a better flexibility as shown in table 6.

Table 4. Pencil hardness on PC for 2 differentUV doses (2 and 4 pass respectively at 12 m/min under 160W/cm, H bulb, in air)

Substrate	500 mJ/cm^2 (2 p at 12 m/min under 120W/cm)			1000mJ/cm^2 (4 p at 12 m/min under 120W/cm)		
Film thickness	6 µm	12 µm	40 µm	6 µm	12 µm	40 µm
PP50S acrylate	F/H	F/H	2H/3H	F/H	F/H	3H/4H
Dendritic acrylate	F/H	2H/3H	4H/5H	F/H	2H/3H	4H/5H
DPHA	F/H	3H/4H	4H/5H	F/H	3H/4H	4H/5H

Table 5. Adhesion on PC (tape test, 0 to 5, 5 best) for 2 UV doses

UV dose	500 mJ/cm^2 (2 p at 12 m/min under 120W/cm)			1000mJ/cm^2 (4 p at 12 m/min under 120W/cm)		
Film thickness	6 µm	12 µm	40 µm	6 µm	12 µm	40 µm
PP50S acrylate	5	5	5	5	5	5
Dendritic acrylate	5	5	5	5	5	5
DPHA	1	2	2	2	3	3

Table 6. T-bend test (cracks appearance at 180 degrees) for 2 different UV doses on PC sheet

UV dose	500 mJ/cm^2 (2 p at 12 m/min under 120W/cm)			1000mJ/cm^2 (4 p at 12 m/min under 120W/cm)		
Film thickness	6 µm	12 µm	40 µm	6 µm	12 µm	40 µm
PP50S acrylate	OK	OK	no	OK	OK	no
Dendritic acrylate	OK	OK	no	OK	OK	no
DPHA	no	no	no	no	no	no

5. Conclusion

The dendritic acrylate based on the new hyperbranched polyester/ether polyol blend is an excellent precursor for the preparation of hard, yet flexible acrylic esters providing the following benefits compared to other high functionality acrylates:

- very good pencil hardness, almost as good as DPHA
- low viscous high functionality acrylate, lower viscosity than DPHA and Di-TMP tetraacrylate
- excellent scratch resistance, as good as DPHA
- excellent water and ethanol resistance
- good flexibility, much better than DPHA
- very good adhesion to plastics like PC

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