Synthesis and characterisation of star branched polyesters with dendritic cores and the effect of structural variations on zero shear rate viscosity

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Dedicated to Professor Imanishi on the occasion of his retirement

Abstract

A series of branched polyesters consisting of poly(ε-caprolactone) (PCL) (degree of polymerisation: 5–200) initiated from hydroxy-functional cores and end-capped with methylmethacrylate have been prepared. The cores were third-generation hyperbranched polyester, Boltorn, with approximately 32 hydroxyl groups, a third-generation dendrimer with 24 hydroxyl groups and a third-generation dendron with eight hydroxyl groups. Finally, a linear PCL was synthesised as a reference material. All initiators were based on 2,2-bis(methylol) propionic acid (bis-MPA). ^{13}C NMR spectra of the polymers showed that those with shorter arms contained unreacted hydroxyl groups on the core. Rheological measurements of zero shear rate viscosity, η_0, showed that the branched polyesters had a considerably lower η_0 than linear polyester with similar molecular weight. The low melt viscosity and the crystallity produced a rheological behaviour suitable for the film formation process for powder coatings. Measurements of mechanical properties of cured films showed that those with low arm molecular weight, M_a, were amorphous while those of high M_a were crystalline. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Star branched; Zero shear rate viscosity; Powder coating

1. Introduction

Powder coatings are based on resins that are solid at ambient temperature and flow at elevated temperatures to form a uniform coating layer. Most are amorphous reactive polymers that cross-link in the molten state to form thermo-set coatings. The use of powder coatings has until recently been limited to the coating of metal substrates since high curing temperatures limited their use on heat sensitive substrates, such as wood and plastic. For conventional systems on the market, the lowest attainable curing temperature is around 120 °C. Curing temperature is determined by the combination of two factors, storage stability and the film formation process. Powder coatings must be storable at 30 °C without fusing of resin particles, thus the glass transition temperature, T_g, of the polymer must be 60 °C or higher. Film formation for amorphous resins requires a temperature at least 50 °C above T_g, giving a minimum curing temperature of about 110 °C [1]. One way to lower the curing temperature is by the introduction of semi-crystalline material with a suitable melting temperature [2]. Low curing temperature also requires an initiating system that is activated at low temperatures while stable at room temperature. This is difficult to achieve with conventional thermal initiators. A possible solution to this problem may be UV-initiation [3,4].

Several other aspects have to be considered when designing semi-crystalline resins for thermoset applications. The synthesis must allow large-scale production and the resin must produce a stable powder using practical methods. Cross-linking must be possible using conventional techniques with the final film exhibiting required properties.

Dendritic polymers [5], comprised of dendrimers and hyperbranched polymers, have been shown to possess unique properties, such as low melt viscosity as a function of molar mass and high solubility in various solvents, compared to their linear analogs [6–9]. Hyperbranched polymers can also serve as scaffolds for the attachment of functional end-groups, such as polymer structures, which can be semi-crystalline [10,11]. The grafting of crystallisable chains to a hyperbranched polymer, resulting in star branched polymers, has also been demonstrated [12].

The rheological behaviour of star polymers is expected to differ from linear and dendritic polymers, since their relaxation modes are different [13]. Entangled star polymers cannot relax through repetition since one end is attached to a 'core'. Instead, the arms relax through primitive path

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fluctuations [14] and constraint release [15]. Primitive path fluctuations, sometimes called 'breathing modes', occur when the polymer arm is drawn back into the tube and then re-extended into a new tube. Constraint release occurs when the surrounding arms fluctuate. The fluctuations lead to tube widening, which is analogous to adding a solvent and is therefore called 'dynamic dilution' [16].

For linear polymers, the onset of entanglement coincides with attainment of critical molecular weight, M_c, which for highly flexible polymers ranges between 300 and 600 atoms in the main chain [17]. Zero shear rate viscosity, η_0, depends on M as $\eta_0 \propto M$ below M_c and $\eta_0 \propto M^{3.4}$ above M_c, for star polymers however, η_0 increases exponentially with molecular weight [18]. The η_0 of a star polymer is not dependent on the total M_w, but on M_a [19]. This makes it possible to increase the molecular weight without affecting the viscosity.

When processing a polymer melt, viscosity is the most important factor to consider since it is the internal resistance to polymer shaping and, in the case of coatings, to levelling. The driving force for levelling is the reduction of the surface tension. Of the parameters affecting levelling, such as viscosity, wavelength, amplitude, mean film thickness, and surface tension, viscosity is the only parameter controlled by molecular architecture [20]. During levelling, the shear rate is very low [21,22], hence η_0 is of critical influence.

This paper reports on results from synthesis and measurements of the zero shear rate viscosity for a series of branched polyesters. The polyesters in this study consisted of poly(ε-caprolactone) initiated from hydroxy-functional cores. The cores were a third-generation Boltorn, commercially available hyperbranched polyester with approximately 32 hydroxyl groups, a third-generation dendrimer with 24 hydroxyl groups, a third-generation dendron with eight hydroxyl groups. Finally, a linear poly(ε-caprolactone) (PCL) was synthesised as a reference material. All initiators were based on 2,2-bis(methylol) propionic acid (bis-MPA). The branched polyesters were finally end-capped with a cross-linkable moiety. Mechanical properties of cured films were also measured.

2. Experimental

2.1. Materials

The hydroxyl-functional hyperbranched, aliphatic polyester (Boltorn™-H30) and 2,2-bis(methylol) propionic acid (bis-MPA) were supplied by Perstorp AB, Perstorp, Sweden. Boltorn™-H30 has a theoretical molecular weight of 3607 g mol^{-1} and an average of 32 hydroxyl end-groups per molecule [10,23]. Benzyl bromide, 18-crown-6 and methacrylic anhydride were purchased from Lancaster. 4-Dimethylaminopyridine, *N,N'*-dicyclohexylcarbo-diimide, *p*-toluene sulfonic acid (*p*-TSA) and 2,2-dimethoxypropane

were all purchased from Acros. 4-Dimetylaminopyridinium 4-toluenesulfonate (DPTS) was prepared according to a literature procedure [24]. Sn(Oct)$_2$, Chromium(III)acetylacetonate and 1,1,1-*tris*(4-hydroxyphenyl)ethane were purchased from Sigma-Aldrich. ε-Caprolactone (ε-CL) was purchased from Acros, distilled and stored under N$_2$(g) prior to use. Irgacure 184™ (1-hydroxy-cyclohexylphenyl-ketone) was obtained from Ciba-Geigy.

2.2. Equipment

^{1}H and ^{13}C NMR were recorded on a ***Bruker AM 400, at 400 and 100 MHz, respectively, using CDCl$_3$ as solvent. For quantitative ^{13}C NMR, chromium(III)acetylacetonate, a paramagnetic substance, was used to reduce relaxation time [25]. The solvent signal was used as the internal standard. Size exclusion chromatography (SEC) was performed using the Waters Model 510 solvent delivery system, Waters 717plus Autosampler automatic injector, PL-ELS 1000 differential refractometer as detector, and three PLgel 10 µm mixed-B columns from Polymer Labs. CHCl$_3$ (1.0 ml min^{-1}) was used as the mobile phase. Calibration was carried out using linear polystyrenes of known molecular weight and dispersity. Millennium version 3.05.02 software was used to process data. Rheology measurements were made using steady shear conditions with a controlled-stress Physica UDS 200 rheometer equipped with cone and plate geometry. The cone had a diameter of 25 mm and an angle of 2°. UV curing was performed on a high-power microwave irradiator from Fusion UV Curing system, using an electrode-free H-bulb regulated by a P300 Power Supply. The spectral range used for curing was between 320 and 390 nm. The dose was measured with an UVICURE® Plus device from EIT Inc. Film thickness was measured with a Mitotoyo micrometer Model: ID-C112B. Dynamic mechanical properties were analysed using a Polymer Laboratories dynamic, mechanic, thermal analyser (DMTA) in tensile mode.

2.3. Synthesis

The synthesis can be divided into three parts: synthesis of core molecules, grafting, and end-capping. The synthesis of benzylidene protected bis-MPA, third-generation dendron and dendrimer was accomplished according to a procedure developed by Ihre et al. [26]. Grafts were obtained by growing ε-caprolactone onto hydroxy-functional cores. Finally, the hydroxy-functional end-groups of poly(ε-caprolactone) were end-capped with methacrylate groups. The macro monomers differed with respect to the length of the poly(ε-caprolactone) grafts.

2.3.1. General procedure for grafting of poly(ε-caprolactone) onto Boltorn™ and dendrimer

Third generation Boltorn™ (2.47 g, ~21.9 mmol hydroxyl groups) was ground in a mortar and then added to a round-bottomed flask. The polyester was dried at 100 °C for at

least six successive cycles of Ar(g)-vacuum followed by a final fill of the flask with Ar(g). Dry ε-caprolactone (50.0 g, 439 mmol) was then added and the temperature raised to 110 °C before a catalytic amount of Sn(Oct)$_2$ (three drops) was added. The reaction mixture was stirred for 20 h until it became a viscous liquid. The polymer was dissolved in THF and precipitated into cold MeOH to give 52.2 g (yield 99 wt%) of a white crystalline powder: ^{1}H NMR (CDCl$_3$) δ 4.18 (m, $-CH_2-O-CO-$, bis-MPA), 4.04 (m, $-CH_2-O-CO-$, ε-PCL), 3.63 (m, $-CH_2-OH$), 2.29 (m, $-CH_2-CO-O-$, ε-PCL), 1.63 (m, $-CH_2-CH_2-CO-O-$ or $-CH_2-CH_2-O-CO-$), 1.37 (m, $-CH_2-CH_2-CH_2-$), 1.22 (m, $-CH_3$). ^{13}C NMR (CDCl$_3$) δ 173.33, 63.94, 62.30, 48.47, 46.40, 33.94, 32.16, 28.17, 25.50, 24.39, 17.60.

2.3.2. General procedure for grafting of poly(ε-caprolactone) to benzylidene protected bis-MPA and dendron

Third generation dendron (76.0 mg, ~0.657 mmol hydroxyl groups) was added to a flask and dried azeotropically at 90 °C by three successive cycles of adding dry toluene and pulling vacuum, after which the reaction flask was filled with Ar(g). ε-Caprolactone (3.0 g, 26 mmol) was added and the temperature raised to 110 °C before a catalytic amount of Sn(Oct)$_2$ was added (1 drop). The reaction mixture was stirred for 20 h until it became a viscous liquid. The polymer was dissolved in THF and precipitated into cold MeOH to give 2.91 g (yield 95 wt%) of a white crystalline powder: ^{1}H NMR (CDCl$_3$) δ 4.18 (m, $-CH_2-O-CO-$, bis-MPA), 4.04 (t, $-CH_2-O-CO-$, ε-PCL), 3.63 (t, $-CH_2-OH$), 2.29 (t, $-CO-O-CH_2$, ε-PCL), 1.63 (m, $-CH_2-CH_2-CO-O-$ and $-CH_2-CH_2-O-CO-$), 1.37 (m, $-CH_2-CH_2-CH_2-$), 1.22 (m, $-CH_3$). ^{13}C NMR (CDCl$_3$) δ 173.33, 63.94, 62.30, 48.47, 46.40, 33.94, 32.16, 28.17, 25.50, 24.39, 17.60.

2.3.3. General procedure for methacrylation

A star branched polyester (45.0 g, ~19 mmol hydroxyl groups) was dissolved in CH$_2$Cl$_2$ in a two-necked round-bottomed flask. Triethylamine (5.69 g, 56.4 mmol) and a catalytic amount of N,N-dimethylamino-pyridine were added to the solution. The flask was equipped with a drying tube and cooled on a water/ice-bath. Methacrylic anhydride (5.79 g, 37.6 mmol) diluted with CH$_2$Cl$_2$ (15 ml) was then added dropwise and the solution stirred at RT overnight. The reaction mixture was further diluted with CH$_2$Cl$_2$ before precipitation into cold MeOH to give 47.9 g (yield 98 wt%) of a white crystalline powder: ^{1}H NMR (CDCl$_3$) δ 6.07 (s, C=CH_2, cis to methyl), 5.53 (s, C=CH_2, trans to methyl), 4.18 (m, $-CH_2-O-CO-$, bis-MPA), 4.04 (m, $-CH_2-O-CO-$, ε-PCL), 3.61 (m, $-CH_2-OH$), 2.29 (m, $-CH_2-CO-O-$, ε-PCL), 1.92 (s, $-CH_3$, methacrylate), 1.63 (m, $-CH_2-CH_2-CO-O-$ or $-CH_2-CH_2-O-CO-$), 1.37 (m, $-CH_2-CH_2-CH_2-$), 1.20 (m, $-CH_3$, bis-MPA). ^{13}C NMR (CDCl$_3$) δ 173.06, 172.38, 171.69, 166.96, 136.10, 135.35,

125.77, 124.85, 68.48, 63.71, 46.18, 33.73, 27.98, 25.16, 24.21, 17.94.

2.4. Viscosity measurements

The zero shear rate viscosity measurements were preformed by measuring viscosity as a function of shear rate. The rheometer surfaces were thoroughly cleaned, a suitable amount of polymer melted onto the lower plate, and the gap between the cone and the plate adjusted to 0.050 mm. Measurements were carried out at 90 °C.

2.5. General procedure for UV-curing of polyesters

The polyester and Irgacure 184™ (1% by wt.) was added to just enough butyl acetate to dissolve the polymer. The mixture was then applied with a 700 μm applicator onto a glass plate. After evaporation of solvent at RT, the film was melted at 70 °C and then immediately UV-cured with five subsequent passes under the UV-lamp, giving a total dose of 500 mJ cm^{-2}. All of the polyesters were cured using the same procedure.

2.6. DMTA measurements

The films were removed from the substrate with a scalpel to a width of 7.5 mm. Film thickness was measured multiple times at various points and an average value calculated. The sample was placed in position, subjected to a superimposed static force and an oscillating strain (0.1%) was applied. The sample was cooled to the starting temperature, -70 °C. The frequency used was 1 Hz and the rate of heating was 2 °C min^{-1}. If excessive creeping occurred during a run, the static force was reduced step-wise until the creeping was eliminated.

3. Results and discussion

3.1. Synthesis

All initiators were based on 2,2-bis(hydroxymethyl)propionic acid, bis-MPA, an AB$_2$-monomer. Boltorn™ was synthesised from bis-MPA and ethoxylated pentaerythritol (four-functional core moiety) where the stoichiometric ratio of bis-MPA to core determined the molecular weight of the final polymer. ε-Caprolactone was grafted onto the hyperbranched polymers according to a procedure previously described by Trollsås et al. [27]. The polymerisation was performed in bulk and different lengths of PCL-chains were obtained by varying the feed ratio between initiating species and ε-caprolactone. The initiator and monomer were carefully dried since traces of water would initiate homo-polymerisation. Data on the synthesised polymers are presented in Table 1.

It has been shown that the ^{13}C NMR shift of the quaternary carbon in the repeating unit of the initiating species is

Table 1
Data of the synthesised polymers

DP, aim	DP, ^{1}H NMR	M_w, ^{1}H NMR (g mol^{-1})	M_w, SEC (g mol^{-1})	M_w/M_n	M_a, ^{1}H NMR (g mol^{-1})	Viscosity (Pa s)
Boltorn-PCL						
5	5	21 870	25 730	1.25	570	1.18
7	8	32 830	32 760	1.28	910	1.32
10	10	40 130	42 950	1.24	1140	2.48
12	13	49 260	48 110	1.20	1430	4.24
15	16	62 050	56 820	1.22	1824	4.69
20	22	83 960	71 940	1.16	2510	10.3
25	22	83 960	81 860	1.35	2510	13.8
30	32	120 490	97 620	1.34	3650	21
35	36	135 100	117 410	1.45	4100	45
40	40	149 710	135 700	1.55	4560	80
45	46	171 620	150 080	1.54	5240	100
45	47	175 270	105 640	1.26	5360	26
50	51	189 880	149 080	1.64	5810	135
50	54	200 840	157 630	1.28	6160	11
55	55	204 500	164 440	1.75	6270	235
55	56	208 150	158 430	1.64	6380	137
70	79	292 150	203 460	1.74	9010	460
Dendrimer-PCL						
15	14	41 100	45 440	1.10	1600	3.30
12	14	41 100	44 450	1.10	1600	3.18
12	14	41 100	46 750	1.17	1600	5.0
10	15	43 840	33 410	1.07	1710	1.34
18	21	60 260	60 340	1.18	2390	4.8
20	24	68 460	64 280	1.12	2740	609
25	30	84 880	76 030	1.13	3420	12.2
30	37	104 030	90 780	1.17	4220	34
35	42	117 710	103 700	1.06	4790	46
40	49	136 860	112 120	1.11	5590	44
45	51	142 340	125 380	1.07	5810	63
60	51	142 340	130 780	1.07	5810	65
Dendron-PCL						
10	11	10 964	20 530	1.10	1250	1.05
10	13	12 790	20 280	1.12	1480	1.13
13	14	13 700	25 540	1.13	1600	1.73
18	15	14 620	25 950	1.17	1710	1.55
15	16	15 530	26 730	1.12	1820	1.58
17	19	18 270	31 160	1.13	2170	2.17
20	20	19 180	33 400	1.14	2280	2.66
20	21	20 100	37 250	1.11	2390	3.85
20	22	21 010	39 080	1.08	2510	5.40
25	23	21 920	38 990	1.16	2620	6.0
22	35	32 880	55 150	1.17	3990	20
35	35	32 880	53 490	1.19	3990	12
37	39	36 530	62 270	1.24	4450	40
40	41	38 360	68 150	1.23	4670	46
40	46	42 920	73 030	1.20	5250	63
80	81	74 880	111 110	1.35	9230	505
Linear-PCL						
10	10	1360	2190	1.12		0.089
15	17	2160	4733	1.13		0.198
14	17	2160	4310	1.18		0.182
16	19	2390	4630	1.15		0.21
20	21	2620	5400	1.10		0.247
20	24	2960	6710	1.15		0.327
24	25	3070	7560	1.13		0.42
22	25	3070	6990	1.22		0.364
30	35	4210	10 850	1.16		0.777
50	45	5350	12 260	1.11		1.10
40	46	5470	12 940	1.11		1.11

Table 1 (*continued*)

DP, aim	DP, ^{1}H NMR	M_w, ^{1}H NMR (g mol^{-1})	M_w, SEC (g mol^{-1})	M_w/M_n	M_a, ^{1}H NMR (g mol^{-1})	Viscosity (Pa s)
50	52	6150	15 120	1.12		1.69
60	54	6380	18 270	1.15		2.76
54	55	6490	14 990	1.14		1.81
60	62	7290	16 840	1.14		2.16
66	66	7750	15 530	1.11		2.7
70	72	8430	19 070	1.19		4.9
80	82	9570	22 830	1.19		7.9
90	96	11 170	24 730	1.21		13.0
100	106	12 310	25 900	1.19		13.7
110	120	13 900	31 010	1.25		26
190	183	21 090	44 180	1.26		120
180	184	21 200	44 320	1.30		134
200	202	23 250	49 560	1.31		215

sensitive to the degree of substitution [28]. The quaternary carbon resonates at 50.6 ppm if both hydroxyl groups are unreacted, at 48.8 ppm if one hydroxyl group remains, and at 46.8 ppm if both hydroxyl groups are reacted. These resonance shifts were useful in assessing the success of the grafting reaction. ^{13}C NMR spectra of the polymers showed that those with shorter arms contained unreacted hydroxyl groups (Fig. 1). Full functionalisation was observed at varying degree of polymerisation (DP) for the various structures (Fig. 2). The dendron and dendrimer were fully reacted at a DP of about 13–15 while the hyperbranched polymer was fully substituted at a DP of about 20. The spectra further showed that in all cases only one of the hydroxyl groups, 48.8 ppm, was unreacted. This lack of functionalisation was probably due to the statistical nature of the reaction since the star polymers with longer arms showed no trace of incomplete end-group functionalisation.

The ^{1}H NMR spectra of the polymers were used to calculate the DP of the PCL-grafts as well as their theoretical molecular weight (Fig. 3). The DP was calculated by comparing the integrals of the protons on the methylene adjacent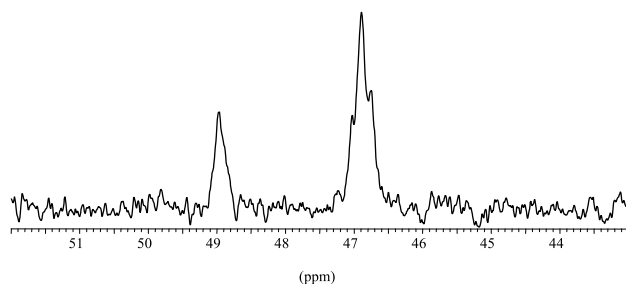 to the hydroxyl end-group relative to those on the methylene next to the carbonyl carbon. It is also possible to perform the calculation by comparison with the methylene next to the oxygen in the repeating unit. This method of calculation, however, is inferior due to the overlapping shift with the core and thus was not utilised. The relative size of the peak from protons next to the hydroxyl group decreased with increasing DP, resulting in reduced accuracy. Thus, the accuracy of the DP value obtained for molecules with high DP was reduced.

Molecular weights determined by SEC deviated from the values derived from the ^{1}H NMR data. This discrepancy was due to a difference in hydrodynamic volume between linear and highly branched polymers, and between polystyrene and poly(ε-caprolactone). Even though SEC molecular weight values were incorrect, SEC data was useful in providing polydispersity data for the polymers. The polydispersities of linear PCL, dendron-PCL, dendrimer-PCL and Boltorn-PCL were within 1.10–1.26, 1.08–1.35, 1.06–1.17 and 1.16–1.75, respectively. In general, polydispersity increased with increasing molecular weight. This was due to the intramolecular and intermolecular transesterification that occurs at high conversion [29].

Attachment of methacrylate moieties to the end-groups of polymers was readily accomplished by base-catalysed transesterification using methacrylic anhydride. Air atmosphere and low reaction temperature were used in order to prevent premature polymerisation, which is a risk when working
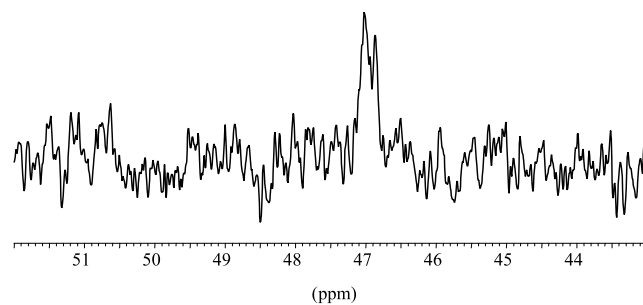

Fig. 1. ^{13}C NMR spectrum of Boltorn-PCL, DP8. The peak at 46.8 ppm shows that there are fully functionalised hydroxyl groups are reacted. The peak at 48.8 ppm shows that there are partially functionalised bis-MPA end-groups. The absence of a peak at 50.6 ppm shows that there are no end-groups where both hydroxyl groups are unreacted. The integral calculation of functionalisation shows that four hydroxyl groups remain unreacted.

Fig. 2. ^{13}C NMR spectra of Boltorn-PCL, DP 32. Only one peak 46.8 ppm shows that all hydroxyl groups have reacted.

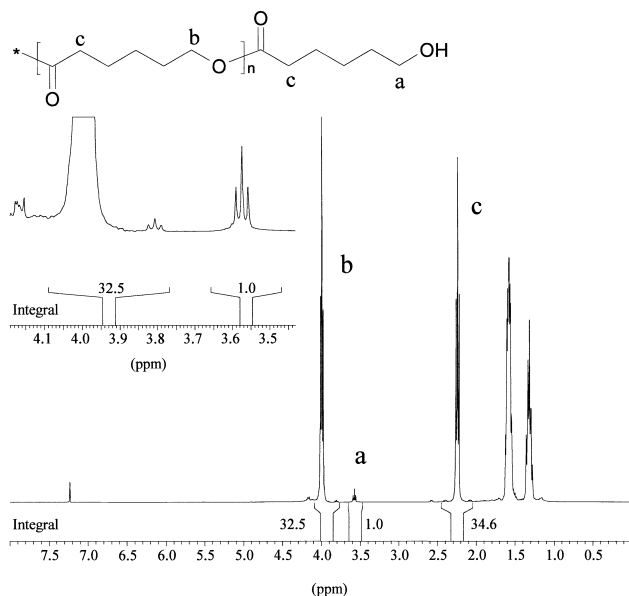Fig. 3. ^{1}H NMR of a Boltorn-PCL with a DP of about 34.

Fig. 5. Viscosity as a function of M_w obtained from SEC. Where ($\triangle$) is dendron-PCL, ($\bigcirc$) is dendrimer-PCL and ($\times$) is Boltorn-PCL.

with highly functional resins. The degree of functionalisation was analysed by ^{1}H NMR-spectroscopy and found to be >90%.

The viscoelastic properties of polymers are strongly influenced by chain entanglement [17]. Chain entanglement occurs naturally in a melt when critical molecular weight, M_c, is attained. The structure also has a pronounced effect on the viscosity of a polymer (Fig. 4). A linear PCL was synthesised and analysed in order to investigate the difference. The linear PCL was found to follow the power law, using the molecular weight obtained from NMR, given by the expressions: $\eta_0 = 7.86 \times 10^{-8} M^{1.92}$ for $M < M_c \cong 5500 \, g \, mol^{-1}$ and $\eta_0 = 7.05 \times 10^{-14} M^{3.52}$ for $M > M_c$. The deviation from $\eta_0 \propto M$ for $M < M_c$ can be attributed to the lack of correction made for the change in the monomeric friction coefficient of M for $M < M_c$ [17,30]. Correc-
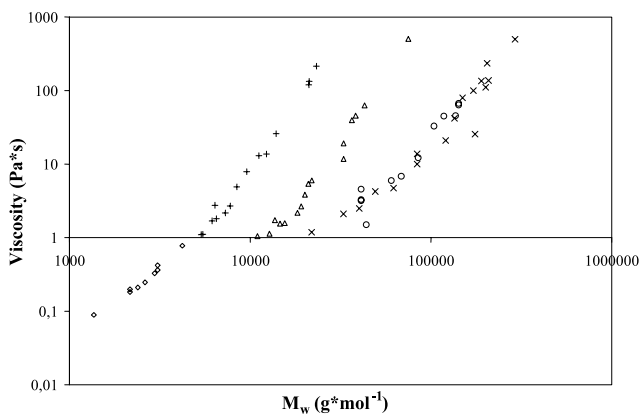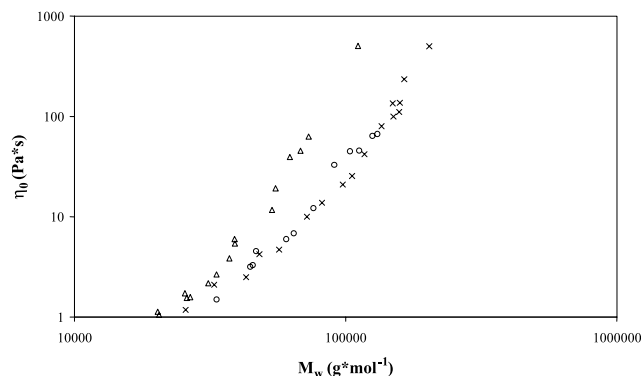

Fig. 4. Viscosity as a function of M_w obtained from ^{1}H NMR. Where ($\diamond$) is linear-PCL, $M_w < M_c$, (+) is linear-PCL, $M_w > M_c$, ($\triangle$) is dendron-PCL, ($\bigcirc$) is dendrimer-PCL and ($\times$) is Boltorn-PCL.

tion of the curve was not within the scope of this study. The M_c-value was equivalent to about 340 atoms (DP $\cong$ 50) in the main chain, which was in the range expected for a highly flexible chain [18]. Using molecular weight values acquired from SEC to obtain M_c gave a value similar to that obtained from ^{1}H NMR after the shift in the SEC data was taken into consideration (i.e. the 'knee' in both curves occurred between the same specific polymer samples).

In the viscosity range of interest for powder coating applications, up to 10–20 Pa s [31], the M_w of Boltorn-PCL was one order of magnitude larger than that of the linear PCL with the same viscosity. The combination of high molecular weight, crystallinity and low viscosity is an advantage for a powder coating resin since previous attempts with low molecular weight crystalline resins have caused problems such as sagging and unwanted penetration of a porous substrate [32]. As mentioned previously, the zero shear rate viscosity, η_0, increases exponentially with molecular weight for star branched polymers [18]. In Fig. 5, η_0 plotted as a function of M_w obtained from SEC measurements. Since the molecular weight range was narrow, it was not possible to accurately distinguish between exponential or power law behaviour for the star branched polyesters. In addition, the relatively broad polydispersity of the samples, which was considerably higher than that normally found in this type of study, also contributed to the difficulty in accurately showing the dependence of η_0 on M_a and M_w.

The η_0 of a star polymer with four or more arms is dependent on the arm length, DP, while independent of the number of arms [33]. The η_0 of dendrimer-PCL and Boltorn-PCL depend on M_w and M_a since the functionality is constant (Figs. 5 and 6). In Fig. 6 η_0 was plotted as a function of M_a and, as shown, the curves do not overlap. This was probably due to the dendritic core molecules having considerably higher molecular weights than the core molecules normally used in rheological studies of star polymers, where the core contribution is considered negligible. In addition, there was some uncertainty regarding the number of hydroxyl groups on Boltorn-PCL. This uncertainty stems from the fact that the structure of

Table 2
DMTA-data of the samples

Boltorn-PCL (DP)	Modulus ($T = -55\,°C$) (MPa)	Modulus ($T = 23\,°C$) (MPa)	Modulus (Rubber-plateau) (MPa)
5	1770	15	15
8	1600	16	16
20	1350	94	2.3
30	380	45	0.9
38	440	79	~1
52	1410	250	~ 1

Boltorn is less exact than a dendrimer. This is due to its less-controlled synthesis, which is a pseudo one-step condensation reaction versus a tedious multi-step reaction. This can cause an error in the M_a since it is calculated using the SEC M_w, except core, divided by the theoretical number of arms.

The temperature at which the measurements were conducted was 90 °C so that the viscosity of all of the samples was in the measurable range of the equipment. In a study by Johansson et al. [34], it was shown that the Boltorn-PCL stars were solid until melting, at which point a rapid drop in viscosity allowed film formation without raising the temperature more than 10–20 °C above melting temperature, T_m.

The dynamic mechanical properties of six Boltorn-PCL films were examined at temperatures between −70 and 100 °C (Table 2). The average film thickness varied between 60 and 130 mm. All samples had onset of T_g close to −50 °C which was as expected for ε-CL based polymers.

The cross-linking reduced the possibility for the PCL-chains to crystallise when the films were cooled. Short PCL-chain resins, DP less than 8, did not crystallise at all in the cross-linked state, while those having longer PCL-chains crystallised to some extent. In previous work, calorimetry data has shown that the degree of crystallisation in the cross-linked films of the long-chained resins was approximately 50% as compared to before cross-linking [34]. The effect of crystallisation in the network is clearly seen in Fig. 7, where the crystalline film maintained a higher modulus above T_g as compared to the amorphous film. The modulus dropped to a lower level above the melting point for the crystalline resins since these resins have a lower cross-link density. The results showed that the structure of a resin has a pronounced effect on the final film properties and, thus, by altering the structure a resin can be tailored for a specific application.

The functionalisation of the end-groups with a cross-linkable moiety makes these types of structures usable as powder coating resins. The rapid decrease in viscosity once molten makes baking and UV-curing at low temperatures possible. This also results in improved levelling since flow in a powder coating is controlled by viscosity. An additional benefit UV-curing offers is control over cross-linking initiation, which can improve levelling. The rheological behaviour during UV-curing has also been studied and showed that the time to gel was less than 2 s and increased with M_w [35]. Residual unsaturation of this type of material is low [34].

4. Conclusion

The M_w of a star branched polyester, with a dendrimer or Boltorn core, is an order of magnitude higher than that of a linear polyester with the same viscosity. This fact, along with the crystallinity and the use of UV-curing, support the possible use of low-temperature curing in powder coating applications for these types of architectures. The viscosity as a function of M_a revealed the influence of the
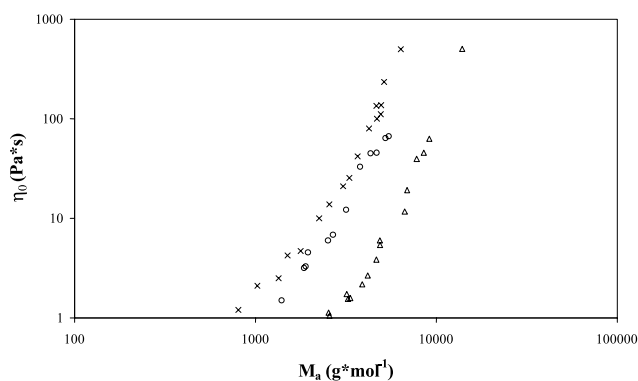

Fig. 6. Viscosity as a function as M_a obtained from SEC. Where ($\triangle$) is dendron-PCL, ($\bigcirc$) is dendrimer-PCL and ($\times$) is Boltorn-PCL.
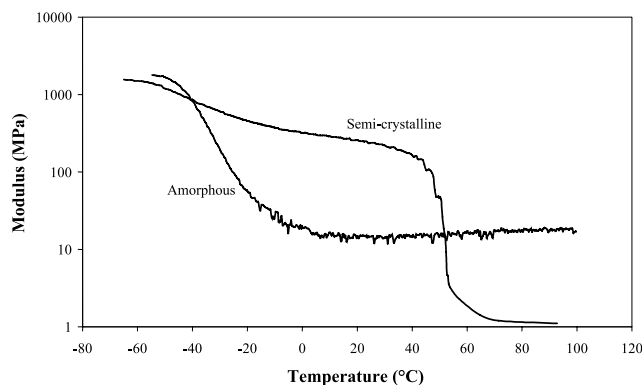

Fig. 7. Modulus as a function of temperature. The semi-crystalline and the amorphous films have a DP of 52 and 5, respectively.

core, and hence functionality, on the rheological behaviour since the M_w of the cores used cannot be considered negligible. This in combination with a narrow range of molecular weights and polydispersity made it impossible to accurately show that the samples displayed rheological properties associated with star polymers. Finally, the dynamic mechanical data showed that the films produced by shorter-armed resins did not crystallise after curing, while those from longer-armed resins did. However, the T_g of this particular system is not ideal for coating applications.

Acknowledgements

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