Synthesis and Characterization of Nonlinear PETs Produced via a Balance of Branching and End-Capping

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ABSTRACT: PET-type polymers have been prepared in the presence of a variety of potential branching agents, such as trimesic acid, and with the control of branching using an end-capping agent, benzyl alcohol. The polymers synthesized have been characterized by dilute solution viscometry, end group analysis, light scattering ($\bar{M}_w$), DSC analysis, and melt rheology. One group of polyesters synthesized with increasing levels of brancher has absolute $\bar{M}_w$ values which increase from ∼10K to 350K Da, and yet despite this, all of the macromolecules display roughly the same limiting viscosity number. Furthermore, though the corresponding zero-shear rate melt viscosity increases with $\bar{M}_w$, the values are far below those expected for analogous linear polymers of comparable $\bar{M}_w$. A second group of polyesters synthesized with a fixed level of brancher and increasing levels of end-capper has a much narrower range of $\bar{M}_w$ values, ∼30K−100K Da, i.e. ∼3−15 times larger than that of a model linear PET. Despite this, these polymers have melt viscosities below that of the linear model. The results are discussed in light of other data in the literature and confirm that branched analogues of linear PET have both lower solution and melt viscosities. While these materials offer the prospect of more facile processing, their solid-state properties may prove to be limited relative to linear polymers, and they may prove more useful as additives rather than stand-alone materials.

Introduction

Poly(ethylene terephthalate) (PET) is a very common commodity polymer used in a variety of everyday objects, from plastic drinks bottles to membrane touch pads on for example microwave ovens.[1−4] Polymer rheology plays a key role in producing many of the final products, and even more sophisticated control of rheology may allow even wider technological application. The manipulation of backbone architecture is one way in which the rheology might be influenced, and in recent years there has been considerable effort directed toward controlling backbone architecture during synthesis of a wide variety of polymers—emphasis being placed on star polymers and dendrimers.[5−9] Indeed that architecture can influence bulk properties is now well established,[10−14] and in the present context it is known that highly branched backbones can give rise to enhanced solubility and reduced viscosity[15−17] when compared to linear analogues.

Some efforts to produce and physically characterize branched PETs have already been reported,[18−25] and indeed such species appear to have been available from time to time from commercial sources.[19] Early work by Manaresi et al.[18] laid a scholarly foundation for the study of branched PET and the correlation of experimental data with theory. The work lacked only data on absolute molecular weights, a point specifically acknowledged by the authors, but nevertheless demonstrated the low intrinsic viscosity, i.e., the low solution limiting viscosity number, LVN, of branched species relative to linear ones, with LVN branched/LVN linear as low as ∼0.2. Likewise, the Newtonian melt viscosity for the branched species was found to be very much lower than that of linear analogues. Complementary work by Langla and Strazielle[20] included the determination of absolute molecular weights from light scattering and membrane osmometry, but the range of molecular weights probed was rather restricted. The overall findings were in line with those of Manaresi et al.[18] The branched PETs produced by Rosu et al.[23] were prepared not only with a branching comonomer but also in the presence of a monofunctional end-capper. The objective was to use rather large levels of brancher but to inhibitit gelation with the end-capper. The materials prepared were deliberately of low molecular weight and were used subsequently in solid phase polymerizations. Branched PETs again with a rather narrow range of molecular weights were also reported recently by Hess et al.[25] These were designed specifically for spinning studies and in particular to allow increased spinning speeds without inducing major changes in fiber properties.

The aim of the present work was to examine a range of polyacids and polyols as statistical branching agents for PETs over a broad molecular weight range and to confirm the influence of branching on polymer solution and melt viscosity over this broader range of polymers. Since branching generally also gives rise to an increase in molecular weight, deconvoluting the influence of molecular weight and branching can be difficult. Consequently, a second series of branched PETs were targeted produced in the presence of an end-capper as well as a branching agent, to produce branched species with a narrower range of molecular weights. Work similar to this was initiated some time ago by Manaresi et al.,[21] but the number of useful samples examined was rather restricted.

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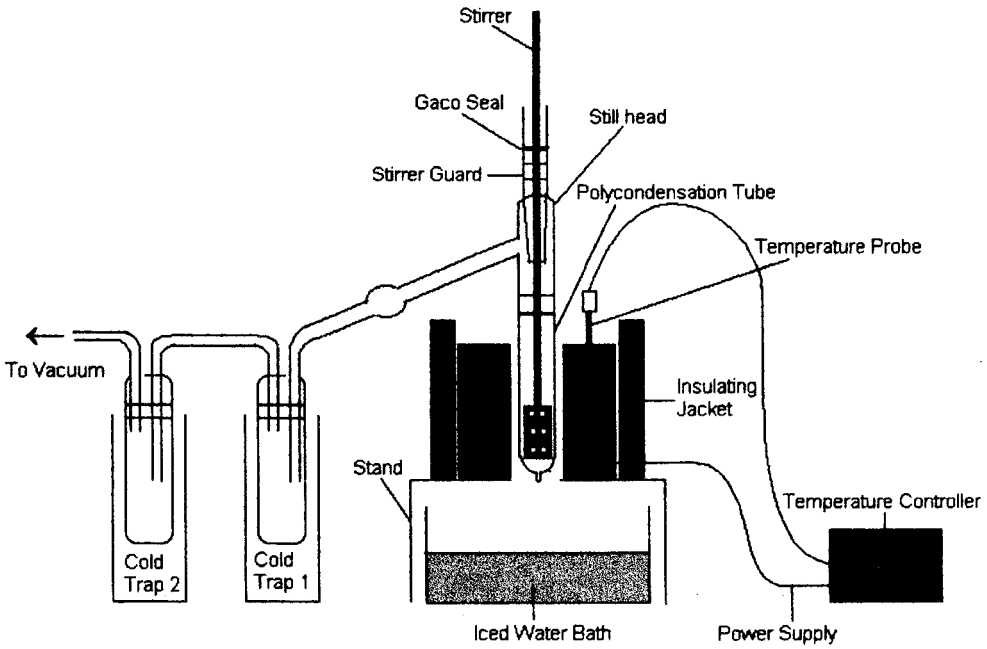

Figure 1. Polycondensation rig.

Experimental Section

Materials. Bis(2-hydroxyethyl) terephthalate (BHET) was initially supplied by ICI and used as received. However, subsequently a batch was prepared in-house from dimethyl terephthalate (600 g, 3.09 mol) and ethylene glycol (1918 g, 30.9 mol) with $Mn(OAc)_2$ (0.24 g, 200 ppm) as the catalyst. The reaction temperature was raised to 220 °C over 2 h while monitoring the volume of CH_3OH distilled off. When 198 mL of the latter had been collected, the molten product was allowed to cool and water (3 L) added to wash away the excess glycol and catalyst fragments. The crushed product was collected and washed with a further excess of H_2O (4 L). Finally, the filtered product was washed with more water (6 × 500 mL) before being freeze-dried. The ^1H and ^{13}C NMR spectra (TFA/$CDCl_3$, 1/10, 270 MH_3) were as expected.

The "monomer" feedstock (i.e., ~7 unit oligomer of BHET) was also supplied from ICI and was prepared by esterification of terephthalic acid with ethylene glycol with simultaneous condensation. Ethylene glycol (26 L) was purged with N_2 and terephthalic acid (60.5 kg) together with sodium hydroxide (3.5 g, 50 ppm) added. The pressure was increased to 3 bar, and the temperature of the oil jacket heater was raised to bring the reaction solution to 255 °C. Water and glycol were continually removed by distillation, and when this slowed, the reactor was vented to atmospheric pressure. The resulting oligomer mixture, i.e., "monomer", was then used as made.

All other monomers and reagents were used as supplied by Aldrich Chemical.

Polycondensation Reactions. Linear and branched PET were produced using BHET or ICI's "monomer" as feedstock and a variety of branching and end-capping agents. Polycondensation reactions were carried out in a custom-built polycondensation rig (Figure 1) on a 150 g scale under a nitrogen atmosphere with Sb_2O_3 catalyst (200 ppm). Branching agents were added at levels of between 2 and 0.0625 wt % and end-capping agents at levels between of 1 and 0.0312 wt %.

The feedstock, branching agent, and end-capping agent as appropriate and catalyst were added to the glass reaction vessel and slowly heated to 240 °C. The mixture was stirred for 40 min under nitrogen. The temperature was then raised from 240 to 290 °C while a vacuum was slowly applied over a period of 1 h down to 0.2 mmHg. The reaction was then stirred for a further hour before the molten product was extruded by gravity into cold water by breaking the glass nipple on the base of the reactor.

Polycondensation Rig. The rig consists of a thick-walled glass reaction tube, with a Quickfit joint at the top and a thin, prescored, glass nipple at the bottom. The vessel is suspended in an iron heating block and connected via a series of pipes and valves to a vacuum pump and a nitrogen inlet. This allows both inert and reduced atmospheres as required. All joints are sealed with standard vacuum grease, except for the joint immediately above the heating block. Two cold traps are employed to collect byproducts and protect the vacuum pump; these contain iced water (trap 1) and liquid nitrogen (trap 2). A Eurostar Power Digital overhead stirrer (IKA Labortechnic) is employed to stir the reaction, using a custom-built stirring shaft. Heating is controlled via a MC810 digital temperature controller (Electrothermic Engineering Limited).

Torque Measurements. The stirrer used in the reaction is equipped with a torque meter. This device, although not capable of measuring the torque absolutely, measures the difference in torque at any given instant, from the initial torque applied to the stirrer. During the reaction, torque readings are recorded throughout by means of an ADC connection to a computer with data logging software.

The torque readings give a guide to changes in the melt viscosity during the reaction and provide a useful comparison of this property between different reactions.

Structural Characterization. a. End Group Analysis. The total number of end groups on the polymer was determined by conversion of the hydroxyl termini to carboxyl groups, addition of excess alkali, and titration with ethanolic HCl.

Hydroxyl groups were derivatized by reaction with succinic anhydride as detailed by Conix.[26] Succinic anhydride (200 mg, 2 mmol) was dissolved in freshly distilled nitrobenzene (20 mL). PET (1 g) and pyridine (1 g, 12.6 mmol) were added, and the mixture was stirred at 190 °C for 1 h. When the solution turned clear, it was cooled and while still warm poured into acetone/water (200 mL, 9:1). A fine white precipitate was formed. The precipitate was washed with acetone (5 × 20 mL) to remove unreacted anhydride and vacuum-dried at room temperature to constant weight.

End group analysis was then carried out as follows: PET (1 g) was dissolved in an *o*-cresol/chloroform mixture (67:20, 20 mL). Ethanolic sodium hydroxide (0.0615 M, 5 mL) was added to the solution, which was then titrated, potentiometrically, with ethanolic hydrochloric acid (0.0531 M). From the end point the total number of terminal groups, E, per 10^6 g of polymer was calculated, where E is the sum of the number of

Table 1. NMR and FTIR Data for PET 1

^{1}H NMR ($CDCl_3$/TFA 1:9 v/v /270 MHz):	δ (ppm)	^{13}C NMR ($CDCl_3$/TFA 1:9 270 MHz)	δ (ppm)	FTIR (liquid film)	ν (cm^{-1})
4H, s, aryl	8.2	*C*O	168.2	OH	3550
4H, s, aliphatic	4.8	*p*-aryl	133.8	aliphatic C−H	2970
		m-aryl	130.5	ester carbonyl	1790
		aliphatic	64.3	1,3,5 trisubstituted aryl	925
				1,4 disubstituted aryl	820

hydroxyl and carboxyl groups at the final extent of reaction, p, achieved in the polymerization. In the case of the difunctional monomer, BHET, and the trifunctional species, benzene-1,3,5-tricarboxylic acid (B3CA), p can be calculated from eq 1.[18]

$$p = 1 - E/10^6[M_b/2 - \rho(M_b/2 - M_t/3)] \quad (1)$$

where M_b and M_t are the molecular weights of the bifunctional and trifunctional segments, respectively, and ρ is the composition parameter given by eq 2.[18]

$$\rho = 3N_t/(3Nt_t + 2N_b) \quad (2)$$

where N_t and N_b are the initial number of tri- and bifunctional monomers, respectively. Analogous equations were used for the other polyfunctional branching agents.

b. FTIR and NMR Spectra. FTIR and ^{1}H and ^{13}C NMR spectra were recorded using a Nicolet 400 D spectrometer and a Bruker DPX 400 instrument, respectively. FTIR spectra were recorded as liquid films. NMR spectra were recorded using a solvent mixture of 90% $CDCl_3$ and trifluoroacetic acid (TFA).

c. Light Scattering. Light scattering experiments were carried out using a Malvern 4700 light scattering instrument, equipped with a variable power (1−150 mW) 488 nm argon laser, the latter being set at 75 mW. PET solutions of 1, 0.8, 0.6, 0.4, and 0.2 wt % in freshly distilled and filtered TFA were prepared. Each solution was filtered 15 times through a 0.22 μm poly(vinylidene difluoride) filter, to remove any dust particles, into "Burchard" cells. The intensity of scattered light from each solution at 25 °C was measured at an angle of 90°. The refractive index (n) and the dn/dc of PET in TFA were determined using a Pulfrich refractometer and a differential refractometer, respectively. Absolute molecular weight values were determined by extrapolation of c/R_{90} against c and application of the Debye equation:

$$Kc/\Delta R_{90} = Hc/\Delta\tau = 1/M + 2A_2c.... \quad (3)$$

where $K = 4\pi^2n^2/N_A\lambda^4(\mathrm{d}n/\mathrm{d}c)^2$, $H = 32\pi^3n^2/3N_0\lambda^4(\mathrm{d}n/\mathrm{d}c)^2$, $\Delta\tau$ = excess turbidity of the solution over the pure solvent, A_2 is the second virial coefficient, M is the mass of particle, ΔR_{90} is excess in Rayleigh ratio at 90°, λ is the wavelength of incident light, and N_A is Avogadro's number.

d. Dilute Solution Viscometry. Standard solutions of each polymer were produced from a stock solution, containing polymer (1 g) in TFA (50 mL, 2 wt %), by serial dilution to give 2, 1, 0.5, and 0.25 wt % solutions.

Viscosity measurement was carried out using an Ubbelohde viscometer (nominal constant 0.009 99 m^2/s^2) at 25 °C. The limiting viscosity number (LVN) was then obtained by extrapolation of η_{sp}/c against c to zero concentration, where η_{sp} is the specific viscosity. $\bar{M}_w$ values were then obtained using the Mark−Houwink relationship for linear PET.[27]

Physical Characterization. a. Differential Scanning Calorimetry (DSC) Analysis. DSC analysis was carried out on selected polymers using a Mettler TA 4000 differential scanning calorimeter. In each case approximately 10 mg of polymer was sealed into an aluminum pan. The pan was placed in the heating chamber of the apparatus on a heat sensor. A reference pan containing an indium sample was placed alongside it on a separate sensor. The DSC trace was recorded through a preset temperature program from −20 to 300 °C at a rate of 20 °C/min. Data for the glass transition (T_g), the crystallization (T_c), and the melting (T_m) temperatures of the samples were deduced from DSC traces.

Table 2. Branching and End-Capping Agents Used in PET Synthesis[a]

code	feedstock	brancher (wt %)	end-capper (wt %)
PET 1	BHET		
PET 2	BHET	2 B3CA	
PET 3	BHET	1 B3CA	
PET 4	BHET	0.5 B3CA	
PET 5	BHET	0.25 B3CA	
PET 6	BHET	0.125 B3CA	
PET 7	BHET	0.0625 B3CA	
PET 8	BHET	0.125 penta	
PET 9	BHET	0.25 B4CA	
PET 10	BHET	0.25 glycerol	
PET 11	BHET	0.125 glycerol	
PET 12	BHET	0.143 dipenta	
PET 13	BHET	0.143 tripenta	
PET 14	"monomer"		
PET 15	"monomer"	0.125 penta	1 BnOH
PET 16	"monomer"	0.125 penta	0.5 BnOH
PET 17	"monomer"	0.125 penta	0.25 BnOH
PET 18	"monomer"	0.125 penta	0.125 BnOH
PET 19	"monomer"	0.125 penta	0.0625BnOH
PET 20	"monomer"	0.125 penta	0.0312 BnOH

[a] BHET = bis(hydroxyethyl) terephthalate; "monomer" = ∼7 unit oligomer of BHET; B3CA = benzene-1,3,5-tricarboxylic acid; B4CA = benzene-1,2,4,5-tetracarboxylic acid; penta = pentaerythritol; dipenta = dipentaerythritol; tripenta = tripentaerythritol; BnOH = benzyl alcohol.

b. Melt Rheology. The steady shear flow curves and dynamic moduli of selected samples were obtained by means of a TA Instruments CSL 500 Carri-Med controlled stress rheometer. Samples were prepared by hot pressing into 2 cm diameter, 500 μm thick disks of polymer using a Graseby Specac constant thickness film maker at 240 °C for 10 min under a load of 10 tons. Samples were then quenched in cold water.

Experiments were carried out at 260 °C. The steady shear stress was determined using a 10-point program at shear rates of 0.2−1 s^{-1}. The zero-shear rate viscosity η_0 was found by extrapolation of the flow curve to zero shear rate. Dynamic moduli were recorded using a 21-point program at angular frequencies of 1−100 rad s^{-1}. Each experiment was carried out in triplicate, and the mean data were obtained.

Results and Discussion

PET was produced in a standard melt polycondensation reaction with real time monitoring of the relative torque applied to the stirrer. The torque readings give a guide to changes in the melt viscosity during the reaction and provide a useful comparison of this property between different reactions.

Polymer yields were essentially ∼100%, and the ^{1}H and ^{13}C NMR data together with the FTIR data (Table 1) are as expected. It was not possible to detect the presence of the branching units from these data.

Three series of PET polymers were studied (Table 2). The first was a set of polymers with varying amounts (0.0625−2 wt %) of trimesic, (benzene-1,3,5-tricarboxylic) acid (B3CA) brancher. The second was a set of

Table 3. Experimental Solution Intrinsic Viscosity and Light Scattering $\bar{M}_w$ Data for Branched PET Produced in the Absence and Presence of End-Capper

code	$\bar{M}_w$ from soln viscosity (Da)	LVN(expt) (dL g^{-1})	$\bar{M}_w$ from LS (Da)	LVN[a] (back-calcd) (dL g^{-1})	g of unentangled	g of entangled
PET 1	6900	0.40	8 000	0.44	0.91	0.97
PET 5	8300	0.45	338 000	4.84	0.09	0.51
PET 6	6600	0.39	73 000	1.81	0.22	0.64
PET 7	5600	0.35	70 000	1.77	0.20	0.63
PET 8	8300	0.45	361 000	5.05	0.09	0.50
PET 9	13000	0.60	386 000	5.27	0.11	0.54
PET 10	15000	0.66	319 000	4.66	0.14	0.57
PET 11	5300	0.34	183 000	3.27	0.10	0.52
PET 12	0	0.01	29 000	1.00	0.01	0.27
PET 13	0	0.01	18 000	0.74	0.01	0.29
PET 14	13000	0.60	13 000	0.6	1.00	1.00
PET 15	2600	0.21	36 000	1.16	0.18	0.61
PET 16	2600	0.21	28 000	0.99	0.21	0.64
PET 17	3900	0.28	28 000	0.99	0.28	0.70
PET 18	3900	0.28	95 000	2.15	0.13	0.56
PET 19	3500	0.26	98 000	2.19	0.12	0.54
PET 20	3600	0.27	133 000	2.67	0.10	0.52

[a] Calculated from $\bar{M}_w$(LS) by substitution in the Mark−Houwink equation and assuming polymer is linear.

polymers produced using a narrower range (0.125−0.25 wt %) of different branching agents, benzene-1,2,4,5-tetracarboxylic acid (B4CA), glycerol, pentaerythritol (penta), dipentaerythritol (dipenta), and tripentaerythritol (tripenta). Finally, a set of polymers was prepared with a fixed level of branching agent (0.125 wt % pentaerythritol) and varying amounts of end-capping agent (0.0312−1 wt % benzyl alcohol).

Trimesic Acid Branched PET. Initial reactions involving 0.5 wt % or greater trimesic acid branching agent (PET 2−PET 4) resulted in a highly cross-linked polymer which wrapped around the reactor's stirrer, causing the reaction to terminate early. PET 2, when isolated, appeared as a hard and strong plastic. It was completely insoluble when added to trifluoroacetic acid (TFA) and merely swelled. PET 3 and 4 were cross-linked to a lesser extent with partial dissolution in TFA. The rest of this set of polymerizations (PET 5−7) proceeded normally, resulting superficially in polymers of similar visual quality and strength to that of linear PET (PET 1). Dilute solution viscosity measurements of the non-cross-linked polymers PET 5−7 gave similar values of LVN to that of linear PET 1 (Table 3). This apparently invariant LVN confirms the similar weak dependence reported by Manaresi et al.,[18] Langla and Strazielle,[20] and more recently Hess et al.,[25] albeit using different solvent systems. The corresponding apparent $\bar{M}_w$ values calculated from the Mark−Houwink equation[27] are also comparable to the value for the linear PET 1. However, the Mark−Houwink relationship is valid only for polymers in a free coil conformation, i.e., linear polymers. Branched species need a more exact method of analysis, which is free from any standards or shape factors. For this reason light scattering was chosen to determine the absolute $\bar{M}_w$ values of the branched species. Table 3 shows the data.

For linear PET 1 there is good agreement with the two $\bar{M}_w$ values found from dilute solution viscometry and light scattering measurements. However, the light scattering derived $\bar{M}_w$ values for the branched species are very much greater (up to 340K) than those calculated from the dilute solution viscosity data. This suggests that the branched nature of these species has lowered the LVN from that expected for linear polymers of equally high molecular weight to a level similar to that of a much lower molecular weight linear polymer.

Table 4. Melt Rheological and DSC Data for Branched PET and Branched/End-Capped PET Samples

code	T_g (°C)	T_c (°C)	T_m (°C)	η_0(expt) (Pa s)	η_0(back-calcd) (Pa s)
PET 1	73.1	132.3	258.9	80	10
PET 5	71.7	132.9	253.7	140	409600
PET 6	73.8	127.1	258.3	120	1800
PET 7	75.0	125.8	260.3	90	1550
PET 8	74.8	144.0	254.7	170	517100
PET 9	72.4	133.4	254.7	260	655400
PET 10	72.9	138.7	251.8	205	333800
PET 11	73.4	138.7	256.1	160	47000
PET 14	72.8	134.7	254.5	80	10
PET 15	67.1	114.3	244.1	∼0	150
PET 16	67.5	116.1	247.5	∼0	60
PET 17	68.3	116.1	247.5	∼0	60
PET 18	67.2	115.0	245.5	5	4880
PET 19	66.0	112.4	242.7	5	5120
PET 20	69.4	124.6	244.9	10	15080

Indeed, substitution of the $\bar{M}_w$ (LS) data into the Mark−Houwink equation[27] and assuming the polymers are linear yields high values (1.8−4.8 dL g^{-1}) for the back-calculated LVN (Table 3).

In principle, similar effects might be expected in the melt viscosity behavior of these branched polymers, since intermolecular entanglements may be reduced relative to linear polymer of the same molecular weight. However, this is not immediately obvious from the experimental data for polymers PET 5−7 in Table 4. The zero-frequency shear rate viscosity, η_0, is comparable to that reported before for branched PET[22,25] but also seems to rise with the level of brancher in the series PET 7 → PET 6→ PET 5. An even stronger variation has been reported before.[18] However, both of these sets of data are complicated because the samples are not only of varying levels of branching but also of varying molecular weight. Indeed, the light scattering determined $\bar{M}_w$ values indicate these species to be of high molecular weight (Table 3), above the entanglement molecular weight, M_c, for all linear polymers.[28,29] Back-calculation of η_0 using a correlation proposed for PET by Manaresi (eq 4),[18] to determine the melt viscosity expected of hypothetical linear polymers, $\eta_{0(linear)}$, of the same molecular weight to the branched species, gives values far greater than those found experimentally for the branched polymer (Table 4). Thus, it can be seen that in reality the branched polymers PET 5−7 do indeed have much lower melt viscosity than linear

Table 5. Parameters Derived from End Group Data for Branched PET Samples

code	PET 1	PET 5	PET 6	PET 7	PET 12	PET 13
no. of end groups, E	78	190	208	273	1263	1017
extent of reaction, p	0.992	0.980	0.979	0.972	0.666	0.731
branching coeff, α	0	0.196	0.100	0.040	0.015	0.013
$\bar{M}_n$ ($\times 10^{-4}$)	2.57	1.15	1.00	0.74	0.06	0.08
$\bar{M}_w$ ($\times 10^{-4}$)	5.11	2.76	2.15	1.51	0.11	0.14
$\bar{B}_n$	0	0.18	0.08	0.03	0.40	0.29

polymers of the same molecular weight.

$$\log \eta_{0(\text{linear})} = -12.96 + 3.54 \log \bar{M}_w \qquad (4)$$

End group analysis of the branched polymers PET 5−7 (Table 5) yielded the data for the extent of reaction, p, from which data for the branching coefficient, α, the number-average molecular weight, $\bar{M}_n$, and the average number of branches per molecule, $\bar{B}_n$, were deduced using eqs 5−7.[18,30]

$$\alpha = p\rho/(1 - p(1 - \rho)) \qquad (5)$$

$$\bar{M}_n = (3M_b + \rho(2M_t - 3M_b))(3 - \rho - 3p) \qquad (6)$$

$$\bar{B}_n = 2\rho(3 - \rho - 3p) \qquad (7)$$

As the level of branching agent B3CA used increases in the samples PET 7 → PET 6→ PET 5, then both the branching coefficient, α, and the average number of branches per chain, $\bar{B}_n$, are seen to rise. However, these data should be taken only as relative values because of the large error associated with the end group analysis—likewise, the corresponding calculated $\bar{M}_w$ values which correlate very poorly in absolute terms with the values determined directly by light scattering.

PET Branched with Other Agents. Further reactions involving a variety of branching agents (B4CA, glycerol, penta, dipenta, and tripenta) (Table 2) with a narrower range of compositions (0.125−0.25 wt %) yielded polymers PET 8−13 which showed similar properties to those prepared using B3CA at similar levels. Light scattering analysis (Table 3) again shows much higher $\bar{M}_w$ than would be predicted from the solution viscosity data. This is clear evidence again that branched species have been produced.

Polymers PET 12 and 13 formed with the polyfunctional branching agents di- and tripentaerythritol, respectively, have extremely low LVN (∼0.01 dL g^{-1}, Table 3), and this together with their physical appearance (a white, crumbly powder), suggests they have very low molecular weight. However, their light scattering data in fact indicate the absolute $\bar{M}_w$ to be ∼4 and 2 times, respectively, that of linear PET 1. These two branching agents would be expected to produce the highest degree of branching for a given weight percent at a given extent of reaction, and the end group analytical data tend to confirm this (Table 5) with $\bar{B}_n$ being 0.40 and 0.29, respectively.

As before, it is possible to take the absolute $\bar{M}_w$ data determined by light scattering and place them in the Mark−Houwink equation[27] to predict the LVN a linear polymer of the same molecular weight would have had. For PET 12 and13 the back-calculated solution LVN viscosities are 1 and 0.74 dL g^{-1}, respectively. Again, these are far greater than the values found experimentally (0.01 dL g^{-1}, Table 3). The corresponding branching factors,[28,29] g (g = LVN branched/LVN linear), for an unentangled system, and g^1 (g^1 = (LVN branched/LVN linear)$^{2/7}$), for an entangled system, are ∼0.01 and 0.28, respectively (Table 3), for both PET12 and PET 13. Other g and g^1 factors are also shown in Table 3, where $g \rightarrow 1$ for a linear polymer. Although these values seem very low, figures as low as 0.19 have been reported before[18] for branched PET, and so there seems to be some consistency between laboratories.

Substituting $\bar{M}_w$ data found by light scattering into eq 4 gives the zero-frequency shear viscosity η_0 of a linear polymer of similar molecular weight to the branched one. The results of these back-calculations are shown in Table 4, along with the actual η_0 values found by experiment for PET 8−13. As with the trimesic acid branched polymers, the data in Table 4 show that the back-calculated η_0 of branched polymers are far higher than those found experimentally. Again, this suggests that linear polymers are much more viscous in the melt than branched polymers of comparable molecular weight. These results bear out the previous findings reported by Manaresi et al.[18] and Hess et al.[25] and fit the pattern arising with other polymers.[31−33]

Branched and End-Capped PETs. Polymers PET 15−20 have been synthesized with a fixed level of pentaerythritol (0.125 wt %) as branching agent and varying levels of benzyl alcohol as an end-capper. The aim here was to produce branched polymers with an absolute $\bar{M}_w$ closer to that of model linear PET than the branched species produced earlier. The hope was that this would then allow unambiguous deconvolution of the effect of increased branching and increased molecular weight on properties such as the solution and melt viscosity. Initially we were concerned that the benzyl alcohol might be ineffective because of evaporative losses, but this fear was not substantiated. Our suspicion is that this reactive benzylic alcohol participates in transesterification much more readily than a nonactivated alkyl alcohol and so becomes incorporated as an end-capper rather early in reactions, hence minimizing its loss. We do not have any direct molecular structural evidence for this, although it is worth noting that this alcohol has been reported previously to function as a satisfactory end-capper.[23]

PET 8 produced with 0.125 wt % pentaerythritol and no end-capper has an absolute $\bar{M}_w$ (LS) of 361 K. Use of benzyl alcohol as end-capper at a level of 0.0312−1.0 wt % reduces the $\bar{M}_w$ (LS) progressively down to ∼30K (PET 17) (Table 3). However, within the range 0.25−1 wt % (PET 15−17) there is little further change, and this may indeed reflect evaporative loss of benzyl alcohol. An optimum ratio of pentaerythritol brancher to benzyl alcohol end-capper is therefore ∼1/2 wt/wt, although of course this factor may well vary for other additives. Again, the solution LVN of all members of this series is in the range ∼0.21−0.28 dL g^{-1}, substantially lower than that of linear PET 1 of ∼0.40 dL g^{-1} with its much lower $\bar{M}_w$ (∼10K).

Some difficulty was experienced in trying to press disks of these samples with sufficient coherence to allow measurement of their melt viscosities, and this is perhaps an indication of the likely bulk properties of these species. In the event the η_0 values for this series proved to be extremely low indeed, 10 to ∼0 Pa s (Table 4), and the effect of increased molecular weight relative to the linear model PET 1 can now be ignored to a first

approximation. Clearly the fall in η_0 is therefore due almost entirely to the branching in these samples. Back-calculation of the hypothetical η_0 of linear polymer analogues with equivalent $\bar{M}_w$ shows very large values, 15 080−150 Pa s, for this series (Table 4).

In the context of balancing the use of branching agents and end-cappers in order to produce high levels of branching without gelation in PET it is difficult to generalize and indeed to comment on the details of the processes involved. Obviously the idealized view for example of equal reactivity of all similar functional groups is almost certainly not applicable, and hence departure from quantitative theoretical predictions is not unreasonable and indeed is probably to be expected. A particularly important issue is the possible differential reactivity of nominally similar functional groups in the brancher and likewise differential reactivity of the end-capper and the primary monomer(s). The present work sheds no light on this; indeed, to carry out experiments in a real system that can do so would be very challenging. Should branched PET systems prove technologically useful, such experiments would be important to pursue.

Thermal Properties. The open literature contains little data on the variation of the melting point, T_m, crystallization temperature, T_c, and glass transition temperature, T_g, of PET as the level of branching is increased. Manaresi et al.[21] reported T_m and T_c to fall with branching while T_g remained almost unchanged. The data however was restricted to only three samples. Rosu et al.[23] likewise found T_c to fall as the level of brancher employed was increased, whereas the data for T_m were ambivalent, showing initially a fall with branching, but increasing again with further branching. Since the latter study involved only a very small molecular weight range, indeed rather small molecular weights (6K−13.5K), generalizing from the data is difficult. Jayakannan and Ramarkrishnan[24] reported that T_m falls with increasing in branching and likewise T_g, while T_c tends to rise. However, the trends were based on only three samples, and no molecular weight data were available for these.

The results from DSC measurements in the present work are summarized in Table 4. Considering first T_m, the variation is not large, but overall there is a tendency for T_m to fall as branching is increased. Since the molecular weight tends to rise simultaneously with branching, the opposite trend might have been expected, but presumably on average branched chains are obliged to pack less regularly than linear ones, hence facilitating melting. For a given molecular weight branched polymer will also have more end groups, and again this will tend to reduce T_m. The biggest change, however, is in the whole group PET 1−12 versus PET 15−20, where there is a fall in T_m of ∼10 °C. Interestingly, whereas the first group are prepared from BHET, the latter are derived from "monomer", i.e., a PET oligomer. Since statistical transesterification should occur during these polycondensation reactions, a systematic variation between these groups might not be expected. However, the experimental data seems to show this fairly clearly. Potentially the distribution of branch points might be more regular in the "monomer"-derived samples PET 15−20 relative to the BHET-derived species PET 5−12, and such enhanced regularity might be expected to increase T_m. However, this runs contrary to the experimental observations.

The crystallization temperature from the amorphous state, T_c, shows a tendency to rise with branching in PET 1−12, but again interpretation of the data is complex because of the concurrent variation in molecular weight. An increase in branching alone might be expected to delay the onset of crystallization, and likewise higher molecular weight would be expected to have the same effect. The most significant trend is the series PET 15−20 showing a fall in T_c of ∼20 °C relative to PET 5−12; i.e., the onset of crystallization from the amorphous state is accelerated in PET 15−20. This may be associated with a more regular distribution of branch points in PET 15−20.

With regard to the glass transition temperature, T_g, data the variation in the group PET 1−12 is not large, and this agrees with earlier observations.[21] On balance there tends to be a fall with branching, and this may be due to somewhat higher free volume created by the local structural irregularity around branch points. A more significant fall does occur, however, with the second group PET 15−20, and within this group also the variation is small. Since T_g tends to be very sensitive to changes in free volume and to the presence of low molecular weight species, which in effect act as plasticizers, the series PET 15−20 may contain systematically a larger proportion of these species. Unfortunately, the data at hand are not sufficiently extensive to demonstrate this, and so this has to remain a speculative observation.

Conclusion

A substantial amount of work has been carried out on the statistical branching of PET by means of standard polycondensation reactions. Branched species were synthesized using a variety of branching agents, and their molecular weight was controlled using end-capping agents. The resultant polymers were shown to be of significantly higher molecular weight than a model linear polymer and to have both lower solution and melt viscosity than linear polymers of equivalent molecular weight. Small amounts of benzyl alcohol resulted in very large differences in molecular weight and inhibited gelation in polymers where high levels (>0.25 wt %) of branching agent were used.

Branched PET of similar molecular weight to commercially produced linear samples may well have poor solid-state properties, and the usefulness of these materials may be as additives rather than stand-alone species.

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