Synthesis and characterization of highly-branched poly(ethylene terephthalate)

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Branched PET samples with a high content of trifunctional comonomer units were prepared by addition of suitable amounts of mono- and trifunctional monomers to dimethyl terephthalate and diethylene glycol. The samples were fully characterized in terms of structural parameters as well as viscosimetric and thermal properties. The properties of the branched samples are in agreement with the expected behaviour on the basis of their microstructure. Equilibrium melting temperatures support the hypothesis of a random distribution of the branching sites.

(Keywords: PET; long branching; random copolycondensation; viscosity; crystallinity; thermal properties)

INTRODUCTION

Aim of the work

Poly(ethylene terephthalate) (PET) is a well-known polycondensation polymer, mostly used in the fibre industry and, in this respect, has been thoroughly investigated by many research groups in the past few decades. More recently, it has drawn increasing attention as a thermoplastic moulding material to be used in new fields of applications, e.g. blow moulding for soft drinks containers. For this specific use somewhat different properties, as compared to those valid for fibre-grade PET, are needed. Specifically, the rheological properties should be adapted to the requirements of the new technologies and this goal can be achieved by means of suitable modifications of PET molecular structure.

The introduction of a controlled amount of long branches on the backbone chain may represent a simple experimental procedure to bring about formation of structural modifications as well as associated changes of the flow behaviour.

The presence of low amounts ($<1\%$) of a reagent with functionality higher than two in the polymerizing system readily leads to long branching formation. However, higher concentrations of this reagent inevitably produce crosslinked structures. Therefore, if relatively high levels of trifunctional comonomer units in the backbone chain without the concurrent gelation reaction are required, a monofunctional reagent has also to be added.

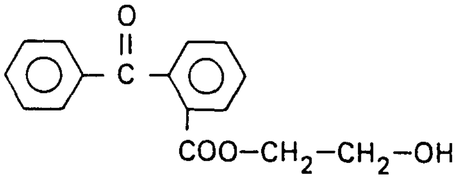
The simultaneous presence of appropriate amounts of mono-, bi- and tri-functional reagents (comonomers) can prevent, at least in principle, gel formation even at medium-to-high conversions.

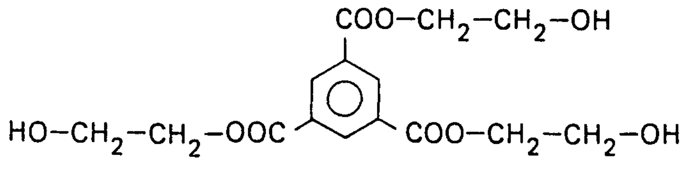
Despite the technological relevance of this subject, few papers have been published so far on the synthesis and/or characterization of branched PET[1-6], of which only one[6] suggests the use of a monofunctional reagent together with a reagent with functionality higher than two.

Against this background we have prepared and characterized branched PET samples, synthesized in presence of high contents ($\geqslant 1$ mol%) of trifunctional comonomer (trimethyl trimesate) as well as monofunctional comonomer (methyl 2-benzoylbenzoate).

Evaluation procedure for chain parameters

The polymerization was carried out in two consecutive steps, ester interchange and polycondensation, according to the general procedure described previously[1]. After the ester interchange step, under our experimental conditions only one type of functional group remains, the OH groups of glycolic esters, i.e.





Polycondensation is of the type 'A reacting with A' and proceeds with the evolution of ethylene glycol.

The basic theoretical concepts concerning multifunctional polycondensation and the criteria for gel

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formation were established several years ago by Flory[7] and Stockmayer[8–10]. Let the composition parameters be ρ_M, ρ_B and ρ_T, i.e.

$$\rho_M = N_M/(N_M + 2N_B + 3N_T) \tag{2}$$

$$\rho_B = 2N_B/(N_M + 2N_B + 3N_T) \tag{3}$$

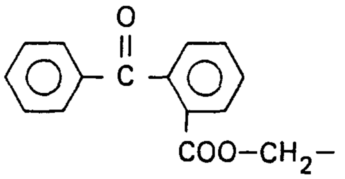
$$\rho_T = 3N_T/(N_M + 2N_B + 3N_T) \tag{4}$$

where N_M, N_B and N_T are the initial numbers of mono-, bi- and trifunctional molecules, respectively.

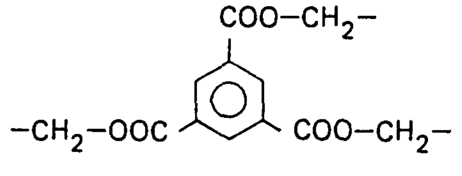
The reaction conversion p, necessary for the calculation of the main molecular parameters, can be obtained from:

$$p = 1 - E\left[\frac{M_B}{2} + \left(\frac{M_T}{3} - \frac{M_B}{2}\right)\rho_T + \left(M_M - \frac{M_B}{2}\right)\rho_M\right] \tag{1}$$

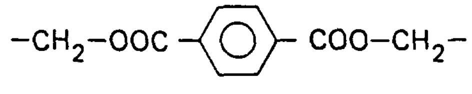
where E is the number of total end groups, in (equiv.) (g of polymer)$^{-1}$ and M_M, M_B and M_T are the molecular masses of mono-, bi- and trifunctional monomeric units, respectively:



$M_M = 239.25$ g mol^{-1}



$M_T = 249.20$ g mol^{-1}



$M_B = 192.17$ g mol^{-1}

Also let X_M, X_B, X_T and W_M, W_B, W_T be the initial molar and weight fractions of mono-, bi- and trifunctional monomers, respectively; assuming that all functional groups have the same reactivity and neglecting intramolecular reactions, we can calculate the number-average molecular mass $\bar{M}_n$[11]:

$$\bar{M}_n = \bar{M}_{n,0}/(1 - p\bar{f}_{n,0}/2) \tag{5}$$

where $\bar{M}_{n,0} = M_M X_M + M_B X_B + M_T X_T$ is the number-average molecular mass of the initial monomeric mixture, $\bar{f}_{n,0} = X_M + 2X_B + 3X_T$ is the number-average functionality of the same mixture.

The weight-average molecular mass $\bar{M}_w$ can be calculated with the above assumptions according to Stockmayer[10] and Munari and Manaresi[11]:

$$\bar{M}_w = \bar{M}_{w,0} + \frac{p\bar{f}_{n,0}\bar{M}_0^2}{\bar{M}_{n,0}[1 - p(\bar{f}_{w,0} - 1)]} \tag{6}$$

where $\bar{M}_{w,0} = M_M W_M + M_B W_B + M_T W_T$ is the weight-average molecular mass of the initial monomeric mixture, $\bar{f}_{w,0} = \rho_M + 2\rho_B + 3\rho_T$ is a kind of weight-average functionality of the same mixture, and $\bar{M}_0$ is given by $M_M\rho_M + M_B\rho_B + M_T\rho_T$.

In the case of polydisperse polymers with randomly distributed trifunctional and monofunctional units, the number-average degree of branching, i.e. the average number of branches per molecule, $\bar{B}_n$, can be calculated as a function of ρ_M and ρ_T and of the conversion, p:

$$\bar{B}_n = 2\rho_T/(3 - \rho_T + 3\rho_M - 3p) \tag{7}$$

EXPERIMENTAL

Materials and synthesis

Dimethyl terephthalate (DMT), ethanediol (EG), calcium acetate and Sb_2O_3 were reagent grade products and were used as supplied. 1,3,5-tricarboxymethylbenzene (TMT) and methyl 2-benzoylbenzoate (MBB), prepared from the corresponding acids by esterification with methanol, were crystallized from methanol twice.

Polymerizations were performed in a 1.8 litre stainless steel reactor, according to the usual two stage equilibrium polycondensation procedure.

In the first stage, at atmospheric pressure and in the presence of calcium acetate as catalyst, methanol was distilled off while the temperature was raised from 130 to about 200°C. At the end of the first stage Sb_2O_3, dissolved in EG, was added as polycondensation catalyst and pressure was reduced to 0.5 mbar, while the temperature was raised to 275°C and maintained at this level until the end of the polymerization.

Polycondensation runs were carried out starting from the following initial compositions:

run BA (3.46, 5.38×10^{-2}, 16.15×10^{-2} and 8.40 mol of DMT, TMT, MBB and EG, respectively, and 3.50×10^{-3} and 0.52×10^{-3} mol of calcium acetate and Sb_2O_3, respectively).

run BB (3.46, 11.66×10^{-2}, 34.92×10^{-2} and 8.62 mol of DMT, TMT, MBB and EG, respectively, and 3.50×10^{-3} and 0.52×10^{-3} mol of calcium acetate and Sb_2O_3, respectively)

run BC (3.30, 25.5×10^{-2}, 24.89×10^{-2} and 8.75 mol of DMT, TMT, MBB and EG, respectively, and 3.50×10^{-3} and 1.03×10^{-3} mol of calcium acetate and Sb_2O_3, respectively).

In the last case (run BC) gelation was reached suddenly after the beginning of the second stage and the polymer could not be recovered.

During a typical polymerization run two or three samplings were taken from the bottom of the reactor at different reaction times (BA_1, BA_2, BA_3, BB_1, BB_2).

A linear PET was synthesized as described above and used as a reference material. Polymer samples were dried at 130°C under vacuum overnight when necessary.

Vapour pressure osmometry (v.p.o.)

Number-average molecular masses were obtained by a Mechrolab 301 A vapour pressure osmometer, using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the solvent at 37°C.

End-group analysis

Hydroxyl plus carboxyl end groups were evaluated by titration of samples obtained by reacting PET, dissolved in nitrobenzene–pyridine (95/5 by vol) at 150–170°C with succinic anhydride, as previously described for poly(butylene terephthalate)[12].

Composition analysis

The composition analysis was done by reacting PET samples with hydrazine hydrate[13]. About 0.08 g of PET was added to a mixture of hydrazine hydrate (2 ml) and DMSO (3 ml) and kept at about 100°C under magnetic stirring for about 3 h. H.p.l.c. analysis of the hydrazinolysis products was performed with a Perkin–Elmer Series Instrument, equipped with a LC-65T u.v. detector at 280 nm and an ODS-MC SIL-X-1 G26X25 column. Methanol–water (45/55 by vol) was the eluting mixture (at 1 ml min^{-1}) and the column was maintained at 55°C.

A calibration against dibenzoyl as the internal standard was obtained, using the products prepared by reacting hydrazine hydrate with DMT, TMT and MBB, respectively. In such conditions, all the products were eluted in *ca.* 7 min and the retention times were 1.27 for DMT and TMT, 3.05 for MBB and 5.53 for dibenzoyl. It can be seen that a good separation, suitable for analytical purposes, could be achieved only for the decomposition product of the monofunctional monomeric units.

Melt viscosity

Melt viscosity values were obtained at 275°C by a Ceast Mod. 6540 capillary rheometer at constant pressure, using a 60 mm long capillary, i.d. 1.5 mm, with a reservoir of 9.5 mm diameter; usually, loads ranging from 1.0 to 5.0 kg were used. For each sample four consecutive test strands were taken; since η values slightly decreased from one strand to the next one, the value of η was obtained by extrapolation to zero time, i.e. at the end of the warm-up period ($\sim$4 min after the introduction of the sample into the reservoir). Since the rate of shear was low in all cases, the measured viscosity can be considered Newtonian.

Dilute solution viscosity

A dilution viscometer of the Ubbhelode type was used. Measurements were carried out in phenol–1,1,2,2-tetrachloroethane (P/TCE) (60/40 by wt) at 30.0°C at four different concentrations for each sample.

Thermal analysis

The thermal properties of as-made and annealed specimens were determined with a Perkin–Elmer DSC II differential scanning calorimeter operating under nitrogen atmosphere and calibrated for the temperature axis with standard samples of indium and tin. Heating rate was 20 K min^{-1} and cooling rate 10 K min^{-1}.

Density

Densities were measured at room temperature in a conventional density gradient column (n-heptane–carbon tetrachloride). Each reported value of density is the average of at least two measurements on different films with the same thermal history. Volume fraction crystallinities were evaluated from the densities through the relation:

$$X_d = (d - d_a)/(d_c - d_a) \qquad (8)$$

where d is the actual density of the specimen, d_a and d_c are the densities of the perfectly amorphous and crystalline phases, viz. $d_a = 1.335$ g cm^{-3} (ref. 14); $d_c = 1.501$ g cm^{-3} (ref. 15).

Infra-red absorption

A Perkin–Elmer 683 infra-red spectrometer was used to analyse all polymer samples. The region between 1000 and 600 cm^{-1} was considered of main interest to measure the crystallinity changes in the samples. Indeed, the band at 973 cm^{-1} is usually attributed to an asymmetric C–O stretch and associated with the *trans* conformation of the –O–C–C–O– group along the PET chain[16,17]. The 896 cm^{-1} band is characteristic of a non-crystallizable *gauche* conformational structure[17].

In agreement with Koening[18] the 795 cm^{-1} band was found independent of crystallinity changes; therefore, this thickness-dependent band was used as an internal standard. An infra-red crystallinity index[16,18,19] was calculated from the 973 cm^{-1} band, whose intensity is very sensitive to the development of order:

$$X_{i.r.} = (A^* - A_a^*)(A_c^* - A_a^*) \qquad (9)$$

where A^* represents the ratios of the absorbances at 973 and 795 cm^{-1}. A_a^* for the amorphous state was directly measured on quenched films with $d = 1.335 \pm 0.001$ g cm^{-3}, while A_c^* was obtained from the A^* vs. density plot for the different samples by linear extrapolation at $d = 1.501$ g cm^{-3}. A_a^* was 0.4 and the extrapolated value of A_c^* was 5.78.

RESULTS AND DISCUSSION

Synthesis

The theoretical treatment of branching, according to Flory and Stockmayer[7–10], predicts that a monofunctional reagent in a system that also contains a trifunctional reagent, shifts the critical conversion, p_c, at which gelation begins, towards higher values. When the molar ration of mono to trifunctional comonomer is $\geqslant 3$ the gel point cannot theoretically be reached. More generally, at a given ρ_T, the same value of $\bar{M}_w$ is obtained for higher conversion, p, in the presence of a monofunctional monomer. This leads to an easier control of $\bar{M}_w$ because p increases more slowly at values closer to one. Practically, this means that in the presence of a monofunctional comonomer, even though gelation can be obtained when $n_M/n_T < 3$, it will occur after a period of time that is longer the closer is n_M/n_T to 3. Thus, the monofunctional monomer facilitates polymerization control well.

These remarks are confirmed by the polycondensation runs: the gel point was not reached at all in run BA, whereas for run BB the gel point was reached only after a long reaction time and rather suddenly for run BC.

Since the equilibrium polycondensation is usually performed at high temperatures, a loss of comonomers, if they have a sufficiently high volatility, is possible. This is particularly true for the monofunctional comonomer. On the basis of its relatively low volatility as well as good reactivity, MBB was chosen as the monofunctional comonomer. The final polymers were tested for MBB content and in all samples only about 70% of the initial content of MBB was found. This result explains the gel

Table 1 Number and weight-average molecular masses and branching parameter $\bar{B}_n$ for branched PET samples

Sample	ρ_M	ρ_T	p	$\bar{M}_n{}^a \times 10^{-4}$	$\bar{M}_w{}^b \times 10^{-4}$	$\bar{B}_n{}^c$	$\bar{M}_n{}^d \times 10^{-4}$
BA_1	0.0156	0.0221	0.9894	1.04	9.15	0.782	0.74
BA_2	0.0156	0.0221	0.9904	1.10	12.1	0.826	0.87
BA_3	0.0156	0.0221	0.9917	1.18	20.6	0.891	0.99
BB_1	0.0415	0.0492	0.9815	0.465	3.45	0.752	0.60

[a] Calculated from equation (5)
[b] Calculated from equation (6)
[c] Calculated from equation (7)
[d] Obtained by v.p.o. measurement

Table 2 Solution and melt viscosities of branched PET samples

Sample	$[\eta]_{30}^{P/TCE}$ (dl g^{-1})	η_0 (Pa s)	$[\eta]_l{}^a$ (dl g^{-1})	$\eta_{0,l}{}^a$ (Pa s)	$[\eta]/[\eta]_l$	$\eta_0/\eta_{0,l}$
BA_1	0.50	55	1.11	4622	0.450	0.0119
BA_2	0.64	103	1.34	10778	0.478	0.0096
BA_3	0.74	195	1.92	69394	0.385	0.0028
BB_1	0.62	35	0.57	133	1.09	0.263

[a] Calculated according to Gregory[20], for a linear PET with the same $\bar{M}_w$ of the corresponding branched sample

Table 3 Glass transition, T_g, crystallization temperature from the glassy state, T_{cc}, and from the melt, T_c, and melting temperature, T_m, of linear and branched PET samples

Sample	T_g (K)	T_{cc} (K)	T_c (K)	T_m (K)
L	352	401	477	526
BA_1	348	412	467	516
BA_2	348	413	463	518
BA_3	351	415	456	519
BB_1	347	415	437	505
BB_2	346	418	447	504

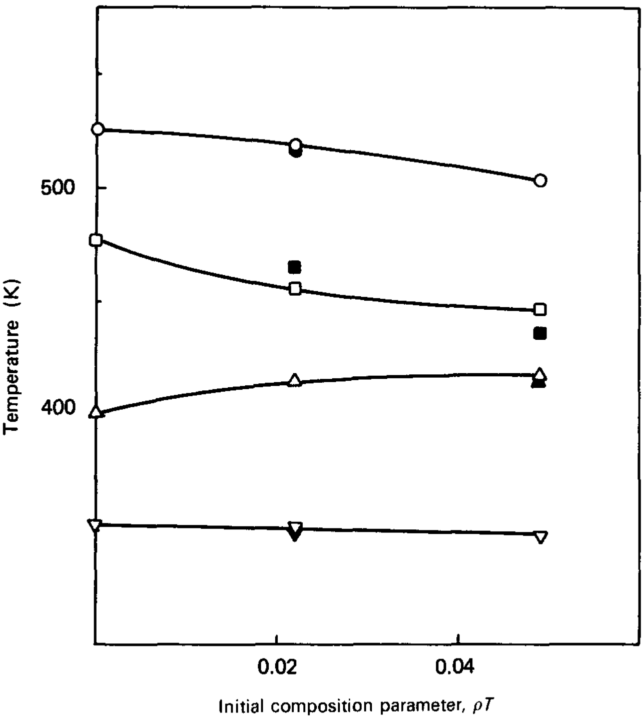


Figure 1 Transition temperatures of PET as functions of the initial composition parameter, ρ_T. ○, melting temperature; □, crystallization temperature from the melt state; △, crystallization temperature from the glassy state; ▽, glass transition temperature. Solid points indicate branched PET sampled during polymerization

fraction in the sample BB_2, whose initial composition, according to theory, should not allow any gel fraction.

The percentage loss of monofunctional comonomer does not increase during the polycondensation step; thus, we can deduce that it occurs only at the beginning of the reactions. In fact, i.r. measurements show that the intensity of the band at 770 cm^{-1}, associated with the out-of-plane bending absorption of the five adjacent hydrogen atoms of MBB in the aromatic ring, remains constant throughout the entire polymerization time.

Chain parameters

In *Table 1*, p, $\bar{M}_n$, $\bar{M}_w$ and $\bar{B}_n$ values calculated from equations (1), (5), (6) and (7) are reported, along with the $\bar{M}_n$ values measured by v.p.o. The difference between $\bar{M}_n$ values obtained by the two methods can be accounted for by a small percentage of cyclic oligomers (~2%) in samples BA_1, BA_2 and BA_3. The presence of a small gel fraction (not detectable by filtration on 0.2 μm pore membranes) can be assumed as a reasonable hypothesis to explain the higher $\bar{M}_n$, found by v.p.o., for sample BB_1.

Viscosity data

The experimental data of melt and intrinsic viscosity of the branched samples are collected in *Table 2* along with the data for a linear PET, with the same $\bar{M}_w$ of the branched ones, as calculated according to Gregory[20].

It must be noted that in samples BA_1, BA_2 and BA_3 intrinsic and melt viscosities are smaller than those of the corresponding linear PET, as happens when only a trifunctional comonomer is added[1]; sample BB_1 shows an anomalous behaviour of $[\eta]$ value: this can be attributed to the possible presence of micro-gel particles, as reported above, or to the greater quantity of mono- and trifunctional comonomers added, which leads to strong modification of the polymer structure.

Thermal properties

Thermal transitions temperatures both in heating and cooling regimes, for various specimens obtained with different amounts of TMT and MBB and at various polycondensation times, are reported in *Table 3* and *Figure 1*.

T_g is substantially unaffected by the variation of the above parameters, whereas melting points and crystallization temperatures are dependent on the concentration of trifunctional groups in the polymerizing medium. Non-isothermal experiments show that crystallization rates are lower for the branched samples than for the linear polymer, both when crystallization takes place in the undercooled melt and from the glassy state.

The melting curve of samples crystallized in isothermal conditions or after annealing exhibits multiple peaks in agreement with the typical behaviour of PET[21–25]. The low temperature peak corresponds to the melting of crystals grown at the crystallization temperature; the high temperature peak is the result of a complex pattern of melting–recrystallization processes that takes place during the thermal scanning and leads to the formation of crystals of higher stability.

In order to evaluate the effect of branching on the melting point depression the Hoffman–Weeks procedure was applied[26] by crystallizing the samples under isothermal conditions for short times in a wide temperature range.

The melting temperatures are plotted in *Figure 2* according to the equation[27]:

$$T_m = T_m^0(1 - 1/\gamma) + (T_c/\gamma) \qquad (10)$$

where γ is the thickening factor. The results reveal a relevant effect of the trifunctional monomeric units on the free energy of fusion.

In *Table 4* the equilibrium melting temperatures, T_m^0, for the various samples are given, together with the melting point depressions evaluated both from our melting point data and from the random copolymer melting equation of Flory[28]:

$$\Delta T_m^0 = T_{m,h}^0 - T_{m,c}^0 = -\frac{R T_{m,h}^0 T_{m,c}^0}{\Delta h_u} \ln n_a \qquad (11)$$

where $T_{m,h}^0$ and $T_{m,c}^0$ are the equilibrium melting temperatures of the homopolymer and of the copolymer, respectively; Δh_u is the melting enthalpy per repeat unit of the crystallizable component, taken as $\Delta h_u = 24.2$ kJ mol^{-1} (ref. 29); and n_a is the mole fraction of the crystallizable component.

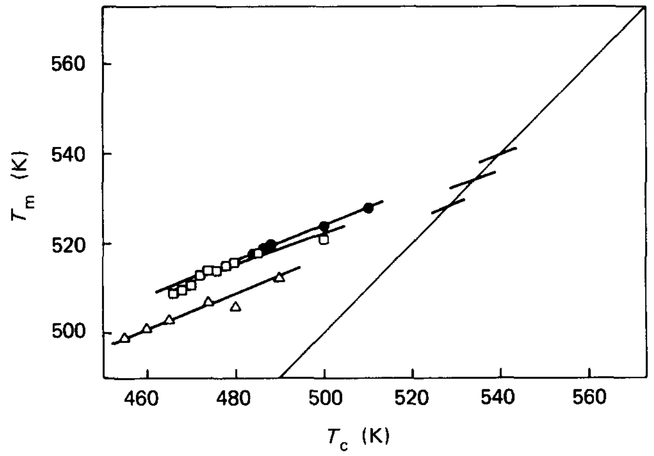


Figure 2 Hoffman–Weeks plot for linear PET (●) and branched PET with $\rho_T = 0.0221$ (□) and $\rho_T = 0.0492$ (△)

Table 4 Experimental and calculated melting point depressions for branched PET samples

Sample	n_a	T_m^{0a} (K)	ΔT_m (K)	ΔT_m^b (K)
L	1	539	–	–
BA_1	0.9542	534	5	5
BA_3	0.9542	534	5	5
BB_2	0.8971	528	11	10.6

[a] From Hoffman–Weeks plots
[b] From equation (11)

Table 5 Melting temperature, T_m, and crystallinity indexes for linear and branched PET samples annealed at different temperatures, T_a, and times, t_a

Sample	T_a (K)	t_a (min)	T_m (K)	$X_d{}^a$ (%)	$X_{i.r.}{}^b$ (%)
L	—	—	—	0	0
BA_3	—	—	—	0	0
BB_2	—	—	—	0	0
L	378	90	396	24.5	22.6
BA_3	378	90	395	24.2	23.1
BB_2	378	90	394	24.8	24.2
L	403	90	407	26.2	24.2
BA_3	403	90	403	27.2	27.7
BB_2	403	90	404	27.3	27.7
L	463	90	474	28.4	29.7
BA_3	463	90	470	32.7	31.4
BB_2	463	90	476.5	30.2	34.6
L	463	450	482.5	34.2	35.5
BA_3	463	450	480.5	33.6	34.7
BB_2	463	450	483	32.3	34.7

[a] From density measurements
[b] From i.r. absorption

The excellent agreement between experiments and theory strongly suggests that the three comonomers are completely miscible in the molten state and that TMT and MBB are completely rejected from the crystal.

It must be stressed that the same equilibrium melting temperature for samples BA_1 and BA_3 proves that polymer composition remains constant during the polycondensation step, as evidenced also by the above composition analysis.

From the data quoted in *Table 5* it is evident that the degree of crystallinity reached by all samples submitted to the annealing treatments is a function of temperature and time, whereas it is almost independent of its specific composition. The data of *Table 5* again suggest that the trifunctional comonomer enables long chain branching, without interfering with the capability of the chain to crystallize.

CONCLUDING REMARKS

The synthesis of highly branched PET, successfully attained by introduction of mono- and trifunctional monomer units in the backbone chain, has provided polymers with expected viscosimetric behaviour. The random distribution of the branches is supported by the trend of the melting temperature data. Long branching does not affect the degree of crystallinity, but reduces the rate of crystallization. Mechanical properties of the branched PET samples show an increase of elastic modulus and a decrease of ultimate elongation, as expected.

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