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Formation of Short and Long Chain Branches during the Free Radical Functionalization of Polyamide 6 in the Melt

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ABSTRACT: Polyamide 6 (PA6) was treated in the melt at 230 °C in a discontinuous mixer with diethyl maleate (DEM) and dicumyl peroxide (DCP). The grafting of DEM to PA6 chains was investigated by ^{1}H NMR analysis, and it reached easily up to 4.5 mol %. The grafted diethyl succinate groups (DES) can successively react with terminal amino groups of different polyamide macromolecules, thus yielding branched polyamide macromolecules. The average degree of branching, determined by titration analysis, is about one per macromolecule under the used experimental conditions and can be improved by further blending with PA6. Thermal analysis of branched PA6 showed lower melting and crystallization temperatures than those of simply processed linear PA6. Blends of unmodified and functionalized polyamide showed a higher viscosity and a more effective shear thinning behavior than the simply processed linear PA6. Experimental evidence was discussed, and a possible reaction mechanism was proposed.

Introduction

The production of new polyamides[1,2] by using peculiar monomer structures could provide an extension of polyamide application field. However, it is necessary to control polyamide molecular weight and structure to obtain a polymeric material with desired rheological and mechanical properties. In particular, star-branched polyamides offer significant reduction in the melt viscosity compared to linear polymers of equivalent molecular weight. This reduction of melt viscosity allows processing at lower temperatures and pressures as well as the possibility to process higher molecular weight polymers.[3] Moreover, reduced viscosity allows also for improved extrudability as well as injection molding of polyamides.

Many papers were published[3−5] about the synthesis of hyperbranched polyamide architectures, whereas only a few papers concern the synthesis of star-branched aliphatic polyamides. Warakomski[6] used polyethylenimine as initiator in the cationic amino-initiated polymerization of ϵ-caprolactam. Risch and coauthors[7] prepared star-branched polyamide 6 samples by a cation-initiated ring-opening polymerization of ϵ-caprolactam with amine initiator functionality of two, three, and six. The thermal properties, with particular reference to the melting transition and its related enthalpy values, changed with respect to the linear polyamide: the crystallization temperatures and the crystallization half-times decreased with increasing number of arms.

On the other hand, anionic polymerization of lactams on the polyamide chains containing *N*-benzoyl side groups makes it possible to manufacture polyamides with branches of other chemical structure than the main chain.[8] In this way polyamide 6-branched polyamide-12 copolymers were successfully synthesized.

Dai[9] obtained polyamide 6 with three branched chains by polycondensation of 6-aminoesanoic acid by using trimesinic acid as molecular weight regulator. This polyamide showed a decrease in relative viscosity with increasing trimesinic acid concentration. At constant MW the increased branching degree makes the macromolecules spherical and noncoilable, thus decreasing the extent of entanglements. The thermal DSC analysis showed also the contemporary lowering of the melting temperature.

The polycondensation of 6-aminoesanoic acid carried out in the presence of terephthalic and trimesitic acid as bi- and trifunctional agents, respectively, was also studied by Yuan.[10] The balance of star-branched fraction polymer and total molecular weight resulted to be fundamental because the increase of the former allows reduction in melt viscosity whereas the increase of the latter leads to good mechanical properties.

Piglowski[11] modified polyamide 6 in the molten state with trimellitic acid (TMA) and *n*-octyl glycidyl ether by reactive processing to insert groups with a long aliphatic chain attaining the reduction of the interfacial tension in polyamide 6/polypropylene blends. Buchenska et al.[12] modified polyamide 6 yarn by radical graft copolymerization of acrylic acid using a dispersing agent and a reaction activator. Some studies have been published concerning the chain extension of polyamide in the melt with chemical agents such as bisoxazoline, maleated polystyrene (SMA),[15] bis(5-(4*H*)-oxazolinones)[16] isocyanate, aldehydes, or phosphines compounds.[17] Polyfunctional agents like trimellitic anhydride,[13] poly(carboxylic acid)-based prepolymers,[14] and poly(methacrylic acid)s,[18] during melt processing of polyamides, have been used to obtain branched polyamides, which display a significantly better flow behavior during processing compared with pure polyamides.

Commercially available polyamide can be easily branched using diesters of carbonic acid, e.g., diphenyl carbonate (DPC) and dimethyl carbonate (DMC), as branching compounds[19] in the presence of suitable catalysts used in the synthesis of

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Table 1. Functionalization with Diethyl Maleate (DEM) in the Presence of Dicumyl Peroxide (DCP) at 230 °C of Polyamide Samples in a Brabender Mixer

run	DEM (mol %)	DCP (mol %)	final torque (N m)	MFR[b]	wt % residual fraction[d]	FD[e]
PA6tq[a]				35.0	99.1	
PA601			0.6	32.6	99.5	
PA602	5.8	0.37	0.6	nd[c]	99.7	3.5[f]
PA603		0.18	1.1	29.2	99.8	
PA604	11.5	0.73	0.5	31.1	98.1	4.3[f]
PA605	5.8		0.5	nd[c]	96.8	

[a] PA6tq is the pure polyamide 6. [b] The MFR of PA604 was determined after purification by acetone extraction. [c] nd = not determined. [d] To boiling acetone extraction. [e] Number of grafted diethyl succinate groups per 100 monomeric units of PA6 (determined by NMR). [f] The standard deviation for the FD values for PA602 and PA604 is 0.2 and 0.1, respectively.

polycarbonates. On the whole in the past few decades the field of polymer modification in the melt has gained great importance allowing the production of polymers with new chemical and physics characteristics, as resulting from the analysis of literature survey. An alternative, practical, and economic route to attain chemical modification consists of the radical functionalization of polymers. As an example, polyolefins are often functionalized in the melt by grafting of unsaturated functional agents with a radical initiator.[20,21] The most common functional agent is maleic anhydride,[22,23] but various monoalkene polymers (HDPE,[24] EPR[25] LLDPE,[26] isotactic and atactic polypropylene[27]) have been also treated with diethyl maleate (DEM) and dicumyl peroxide (DCP). The extension of functionalization to condensation polymers can be an innovative and promising tool to modify their macromolecular structure by introducing suitable functional groups.

Anyway, free radical processes can be responsible for side reactions as degradation or cross-linking.[28] In the case of polyamide 6[29] the oxidation at high temperature (>120 °C), e.g. during processing,[30] is responsible for molecular weight decrease with formation of aldehyde, azomethine, or unsaturated terminal groups as well as drop of tensile properties and yellowing.[31]

In this context the present paper reports for the first time about the free radical grafting of PA6 in the melt by using diethyl maleate (DEM) and dicumyl peroxide (DCP) as a way to prepare new functionalized reactive PA6. Evidence about the reaction of diethyl succinate groups grafted on the PA6 chains with the amino polyamide terminal groups to produce long-branched macromolecules is reported.

Experimental Part

Materials. Polyamide 6 (Ultramid-BASF B3S, $M_n = 20\,000$ as determined by titration) was used as provided without further purification. Diethyl maleate (DEM, Aldrich) was distilled under vacuum (0.33 mmHg, at 53 °C). Dicumyl peroxide (DCP, Aldrich) was used without further purification.

Melt Processing. Polyamide 6 was treated at 230 °C in a Brabender Plastograph (model OHG47055) discontinuous mixer with a 30 mL mixing chamber (Table 1) in which counter-rotating blades rotated at a shear rate of 30 rpm, while nitrogen was continuously flowing during blending. The polyamide polymer was introduced in the mixer at 230 °C under nitrogen flow; after the stabilization of the torque value (typically about 1 N m at 2 min), the solution obtained by dissolving solid DCP into liquid DEM was quickly added. The total experiment time was 10 min.

The samples were collected, milled, and extracted 8 h with boiling acetone in a Soxtech device to remove unreacted molecules and low-molecular-weight products.

Measurements. Infrared spectra were recorded with a Perkin-Elmer 1330 Fourier transform infrared spectrometer on 100−300 μm films obtained by compression-molding, at 230 °C for 5 min setting a pressure of 22 MPa.

^1H NMR and ^{13}C NMR spectroscopy analysis was carried out with a Varian Gemini-600 spectrometer at 600 MHz by dissolving about 35 mg of polyamide 6 samples in deuterated formic acid (DCOOD).[42]

Quantitative determinations of end $-NH_2$ and $-COOH$ groups of polyamide samples were carried out by titration.[43] About 1 g of each sample was dissolved in 70 mL of benzyl alcohol at 150 °C under nitrogen flow. After adding 20 mL of a mixture methanol/water 2:1 v:v, the resulting solution was titrated with a 0.02 N KOH solution in ethylene glycol (this solution was daily standardized against a 0.0196 N hydrochloric acid solution) using phenolphthalein as the indicator to determine the concentration of $-COOH$ functional groups. In the same way the concentration of $-NH_2$ groups was determined using a 0.0196 N hydrochloric acid solution with bromophenol blue as indicator.

The intrinsic viscosity measurements were performed with a capillary viscometer at 25 °C using dilute *m*-cresol solutions (<0.3 g/dL) of acetone-extracted samples. Intrinsic viscosities were extrapolated by using Huggins and Kraemer equations.[39]

The melt flow rate (MFR), expressed in g of material per 10 min, was determined with a CEAST module melt flow instrument PIN 7026 equipped with “VisualMELT” software which provides melt volume rate (MVR) data, by collecting the position of the piston as a function of time during the test. The melt flow rate was measured at 235 °C, with a weight of 2.16 kg (ASTM D1238), following an ISO1133A standard procedure. It consists of measuring the time necessary for the piston to pass through two standard points of the heated tubular cavity of the equipment while the polymer melt is flowing through a standard nozzle. The samples were kept for 3 h in a 110 °C preheated oven before the MFR test to remove humidity.

Rheological measurements were carried out with a Haake RheoStress RS150H rheometer in the plane-plate geometry (20 mm diameter, 1 mm gap) at temperature 508.2 K under highly pure nitrogen flow. The sample temperature was stable within 0.1 K. Data were collected using a frequency sweep experiment from 24.4 to 0.1 Hz (5% strain). Samples were dried at reduced pressure (0.1 mbar) for 6 h before rheological measurements.

Standard differential scanning calorimetry (DSC) thermal analysis was carried out with a Perkin-Elmer DSC7 differential scanning calorimeter equipped with CCA7 device for low temperatures. The temperature range was 20−250 °C, and the scanning rate was 10 °C/min. Calibrations were made using In and Zn standards. The successive self-nucleation and annealing DSC (SSA-DSC)[32] was performed at 10 °C/min, using a isothermal time of 5 min in the range showed in the Figure 1, where T2 was the temperature at which the sample is completely in the molten state, the lowest temperature of each cycle is well below the crystallization temperature T1, and the first isothermal step below T2 (TS1) is set at the lowest end of the temperature range yielding self-nucleation without annealing (domain II according to Fillon et al.[32]). In the standard procedure, each isothermal step is equally spaced with $\Delta T = 5$ °C.

Results

PA6 Functionalization. Polyamide 6 samples were treated with the modifying agents in a discontinuous mixer (Brabender)

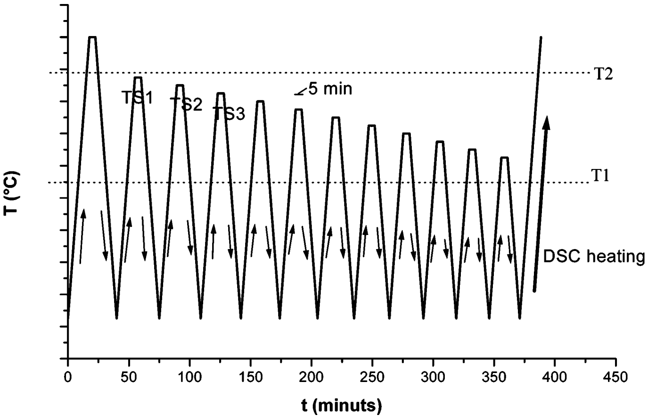


Figure 1. Thermal treatment of SSA-DSC: T1−T2 range of the melting peak of PA6 samples.

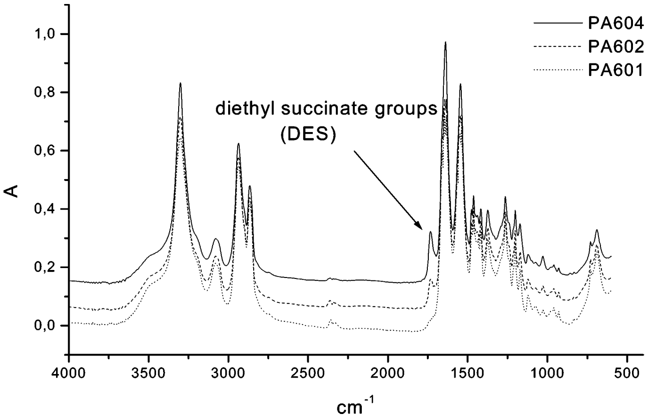


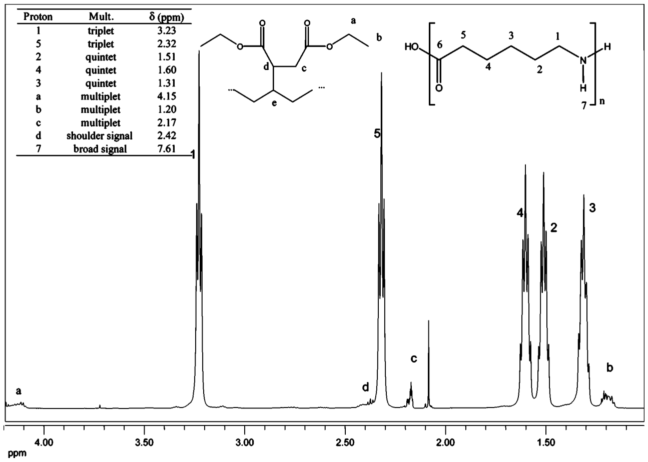
Figure 2. FT-IR spectra of only processed (PA601) and DEM functionalized (PA602 and PA604) polyamide 6.

that provides in real time torque and molten polymer temperature values; in this way it was possible to follow the rheological changes occurring in the melt as the consequence of reagents addition, and the final torque values are reported in Table 1, where the DEM and DCP contents were reported in percentage by moles with respect to the number of polyamide 6 units.

After the above treatment the polyamide samples were extracted with boiling acetone to remove low-molecular-weight products and in particular the unreacted diethyl maleate and the peroxide decomposition products (Table 1). The residual fractions (the polymeric samples) were analyzed by FT-IR spectroscopy (Figure 2): both reacted samples (PA602 and PA604) showed a characteristic band at 1736 cm^{-1}, which can be attributed to the ester C═O stretching of the grafted DES groups.

NMR Analysis. The ^{1}H NMR spectra (Figure 3) showed the presence of the 4.15 ppm resonance (resulting from $-CH_2-$ protons in ethoxyl groups), confirming the occurrence of the grafting reaction. From the integral values, the functionalization degree (FD), defined as the number of grafted diethyl succinate groups (DES) per hundred PA6 units, can be calculated (see data in Table 1).

The study of the spectrum by heteronuclear single quantum correlation (HSQC) NMR technique allowed to attribute the 2.17 ppm signal to the c CH_2 (scheme of Figure 3) because of the direct connection to a 29.05 ppm in the ^{13}C spectrum. Moreover, a further analysis showed that the signal at 4.15 ppm is connected to different types of β-position carbon atoms signals, at 13.4 ppm (CH_3 group) and 174.7 ppm (C═O group), respectively (Figure 4).



Proton	Mult.	δ (ppm)
1	triplet	3.23
5	triplet	2.32
2	quintet	1.51
4	quintet	1.60
3	quintet	1.31
a	multiplet	4.15
b	multiplet	1.20
c	multiplet	2.17
d	shoulder signal	2.42
7	broad signal	7.61

Figure 3. ^{1}H NMR spectrum of DEM functionalized polyamide 6 (PA604) in deteurated formic acid (DCOOD) and main signal assignments.

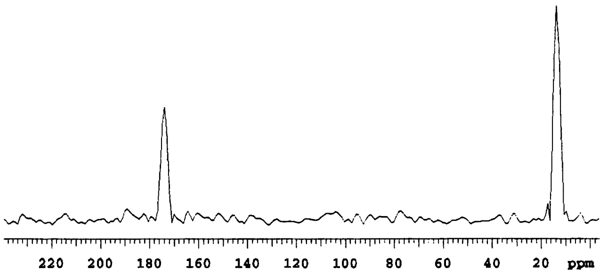


Figure 4. ^{1}H-β^{13}C HSQC analysis of the 4.15 ppm signal.

Table 2. Theoretical Values of Chemical Shifts for c and d Carbons

grafting position	δ CH d (ppm)	δ CH_2 c (ppm)
1	39.4	28.7
2	36.4	29.9
3	37.5	30.3
4	40.0	30.1
5	33.9	32.2

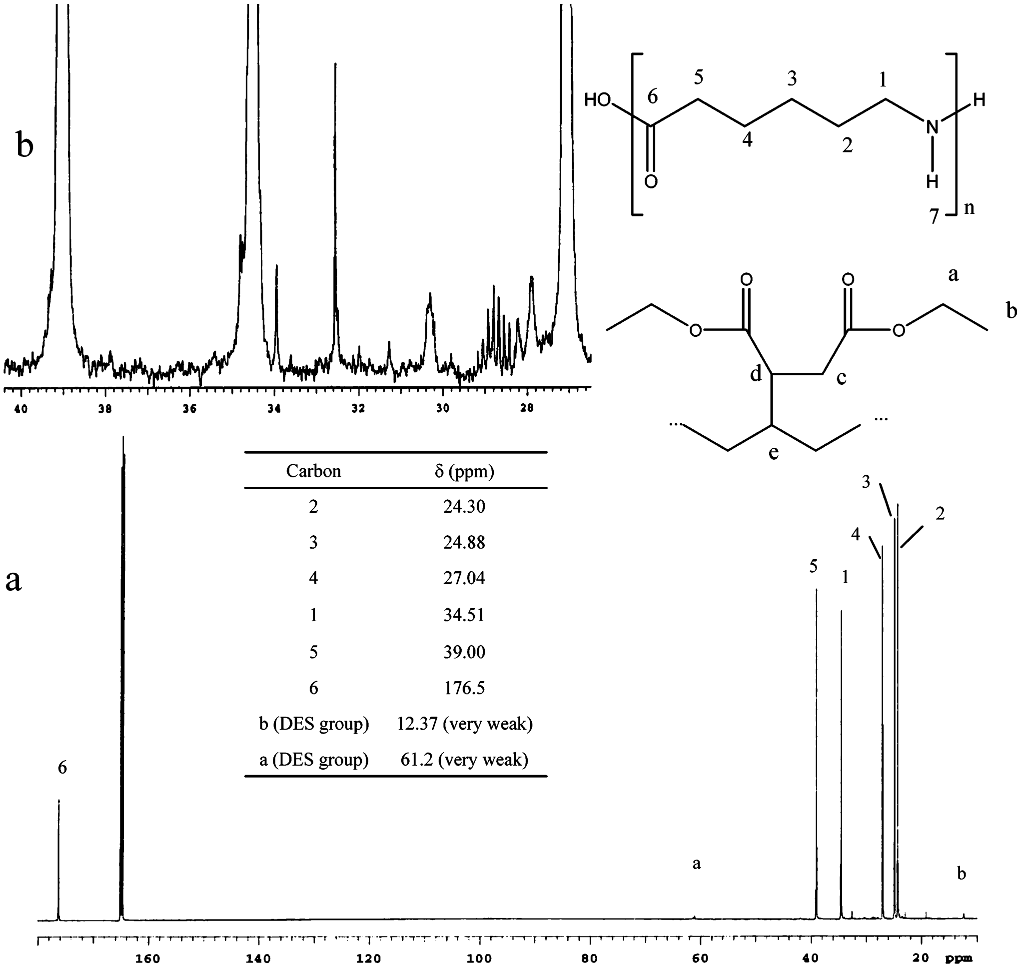
The ^{13}C NMR spectra (Figure 5) showed six main bands that result from carbon atoms in the PA6 unit. In the spectrum of the modified sample very weak signals at 61.2 and 12.37 ppm could be noticed and attributed respectively to the CH_2 (a) and CH_3 (b) carbon atoms of grafted ester units.

The theoretical chemical shift of c and d carbons was calculated by applying additive rules[33] (Table 2) by considering the different grafting position of the DES group on the PA6 unit (1−5).

In the ^{13}C NMR spectrum the presence of many different signals in the 28−31 ppm range (Figure 6b) were in agreement with the grafting of DES groups to $-CH_2-$ in different positions of the polyamide unit. Anyway, more intense signals at 32.5 and 33.9 ppm evidenced the preferential grafting on the 5-position, probably thanks to the beneficial effect of the adjacent electron attractive −C═O group which makes the radical site particularly reactive in the addition to DEM.

The chemical shift signals in 26−42 ppm range and the presence of two weak but evident signals at 176.8 and 179.9 ppm (1′ and 2′ carbons of Figure 6a, respectively) indicated the formation of a succinimide ring.[34] Also, the presence of a weak signal in the ^{1}H NMR spectrum at 3.48 ppm (3′ protons triplet), with a J value of 7.2 Hz was a further confirmation of the formation of such succinimide ring (Figure 6b).

The ^{1}H and ^{13}C analysis was also carried out on PA6 treated with DEM but without peroxide (PA605). The ^{1}H spectrum (Figure 7) shows very weak signals at 6.7−7.1 ppm due to



Carbon	δ (ppm)
2	24.30
3	24.88
4	27.04
1	34.51
5	39.00
6	176.5
b (DES group)	12.37 (very weak)
a (DES group)	61.2 (very weak)

Figure 5. (a) ^{13}C NMR full spectrum of DEM functionalized polyamide 6 (PA604) and spectra main signals assignments. (b) Enlargement in the 28−40 ppm range.

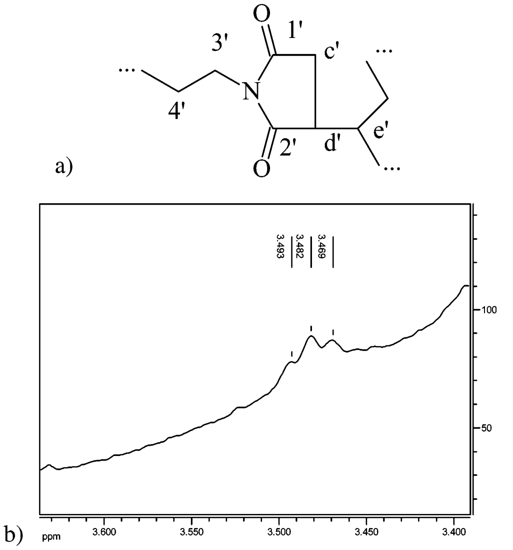


Figure 6. Succinimide structure and ^{1}H NMR enlargement with signal due to 3′ protons.

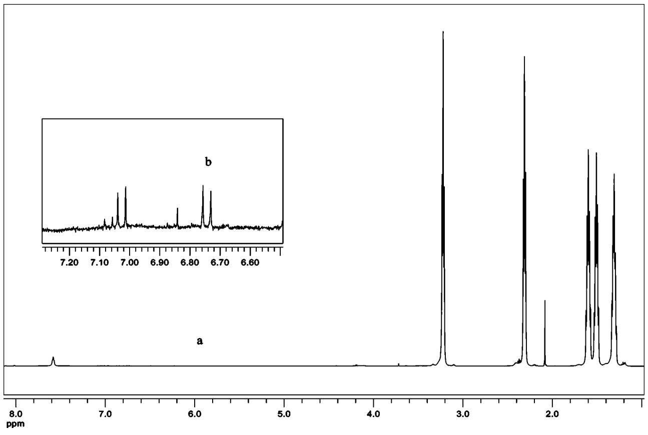


Figure 7. ^{1}H NMR spectrum of polyamide 6 processed with DEM alone (PA605) (a) and enlargement (b).

protons on C═C double bonds, not detected in the PA604 spectrum. The value of the coupling constant is 15.6 Hz, in good agreement with this assignment. The PA605 ^{13}C spectrum showed a lower number of signals than in PA604 in the range 28−31 ppm (Figure 8), in agreement with the absence of DEM grafting on the polyamide chain. Moreover, the 116 ppm signal can be attributed to the C═C double bond carbons. The presence of a weak band in the ^{1}H NMR spectrum at 3.48 ppm with $J = 7.2$ Hz is in agreement with the formation of a maleimide ring.

Titration of End Groups. The polyamide samples were analyzed by titration of end groups (−COOH and $-NH_2$): both −COOH and $-NH_2$ concentrations in processed polyamide either in the absence (PA601) or in the presence of peroxide (PA603) were lower than those determined for the pristine PA6 (PA6tq). When DEM is present in the processed mixtures (runs PA602 and 04), the $-NH_2/-COOH$ ratio is <1. $\overline{M_n}$ were calculated from $[NH_2]$ values with the hypothesis that each macromolecule has one NH_2 group with the only exception of

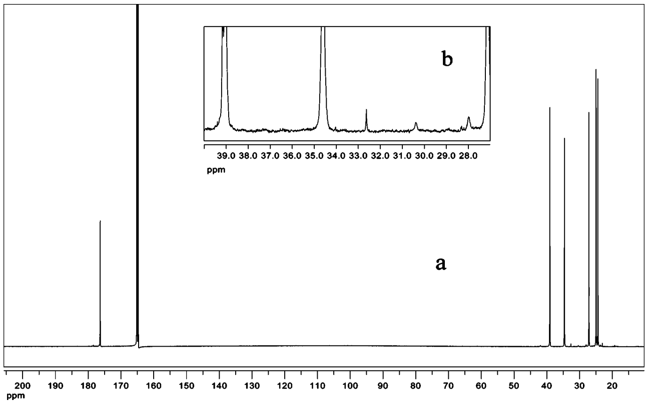


Figure 8. ^{13}C NMR spectrum of polyamide 6 processed with DEM alone (PA605) (a) and enlargement (b).

Table 3. −COOH and −NH$_2$ Terminal Groups Concentration by Titrations Results and Corresponding Intrinsic Viscosities of Processed PA6 Samples

samples	DEM/NH$_2$ mole ratio	[COOH], mequiv/kg	[NH$_2$], mequiv/kg	$\overline{M}_n$, g/mol	$[\eta]_M$ [d]
PA6tq	0	50	51	19 600[b]	1.28
PA601[a]	0	27	29	34 500[b]	1.64
PA603[a]	0	24	22	45 000[b]	1.50
PA602[a]	10	19	11	90 000[b]	1.48
PA604[a]	20	21	9	110 000[b]	1.74
PA605[a]	10	40	12	25 000[c]	1.26

[a] Processed samples are previously extracted with boiling acetone. [b] Calculated on the basis of the amino end groups concentration by assuming one −NH$_2$ group per macromolecule. [c] Calculated on the basis of the carboxyl end groups concentration. [d] $[\eta]_M$ is the average value of intrinsic viscosities calculated by both Huggins and Kraemer methods.[39]

run PA605 where COOH concentration value was used. The intrinsic viscosity values were also determined (Table 3). A decrease of −NH$_2$ concentration with respect to PA6tq was also observed when DEM alone was added during the processing (PA605).

The standard DSC analysis showed that the melting and crystallization temperatures of the samples decreased as the consequence of functionalization (Figure 9 and Table 4). The enthalpy values associated with these transitions also decreased.

The samples were analyzed by DSC and successive self-nucleation and annealing DSC (SSA-DSC) which is essentially a thermal fractionation method based on the sequential application of self-nucleation and annealing steps to a polymer sample[32] (see Figure 1). After thermal conditioning a final DSC heating run reveals the distribution of melting points induced by the SSA treatment as a result of the heterogeneous nature of the chain structure of the polymer under analysis.

The self-nucleation temperatures Ts1, as determined separately by self-nucleation experiments,[35] were set at 222 °C for the nonfunctionalized samples and at 220 and 218 °C for samples PA602 and PA604, respectively. However, to better compare the thermograms resulting from the various SSA-DSC runs, all the remaining isothermal steps were set at the same temperatures for all the samples. Therefore, the final DSC curves reported in Figure 9 reflect both the differences in the crystallinity and morphology of the various samples and the reduced temperature gap between the isothermal steps Ts1 and Ts2 in the case of the functionalized PA602 and PA604.

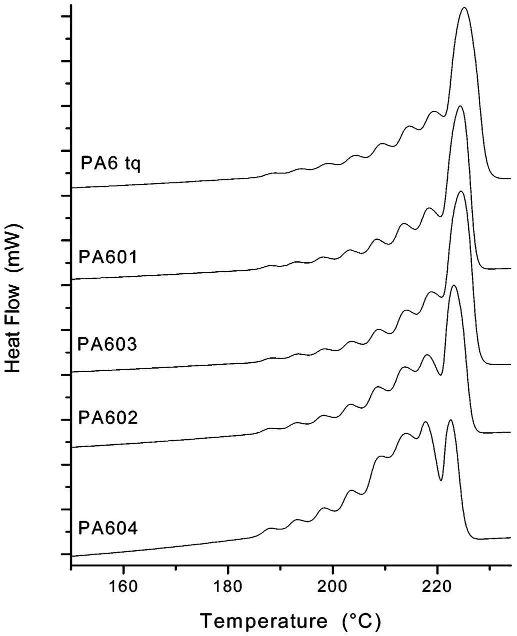


Figure 9. SSA-DSC curves pure polyamide (PA6tq) and melt-processed samples. PA602 and PA604 are the DEM functionalized samples.

Branched and Functionalized Polyamide Reactivity in Neat Polyamide. The functionalized and branched polyamide 6 (run PA604) purified by extraction with acetone was blended with the original PA6 at different weight ratios under the same conditions adopted for the functionalization runs (Table 5) with the aim to study the reactivity of DES groups grafted to functionalized polyamide toward PA6 terminal groups and the consequent evolution of the macromolecules structure.

As a consequence of the addition of PA604 to PA6 up to 65 wt %, a decrease of MFR with respect to PA6 processed in the absence of additives (PA601) was noticed. At the same time a decrease of −NH$_2$ concentration was observed, whereas the concentration of −COOH remained constant.

Rheological measurements on PA601 and PA-25 (PA6/PA604 75:25 by weight) were performed in the frequency domain, which provides information about the moduli and the viscosity. According to the Cox−Merz rule,[36] the steady shear viscosity vs shear rate curve (η vs $\dot{\gamma}$) has the same shape and values as the complex viscosity vs angular frequency curve ($|\eta^*|$ vs ω) if they are compared at $\dot{\gamma}$ (s^{-1}) = ω (rad/s) (Figure 10). On this basis the curves in Figure 10 show that the $|\eta^*|$ of PA-25 is higher than that of PA601 in the investigated ω range. Moreover,

Table 4. Results of Standard DSC Analysis of Pure Polyamide (PA6tq) and Melt-Processed Samples

	crystallization			melting		
sample	T_c, peak (°C)	T_c, onset (°C)	ΔH_c (J/g)	T_m, peak (°C)	T_m, onset (°C)	ΔH_m (J/g)
PA6tq	189.4	193.6	−68.8	221.0	210.1	69.3
PA601	189.2	193.2	−68.2	219.9	209.2	70.6
PA603	189.4	193.6	−67.5	220.2	209.3	69.3
PA602	188.4	192.2	−65.1	218.7	207.5	64.2
PA604	185.6	189.7	−59.6	217.0	204.5	59.2

[a] Calculated in the range between 155 and 200 °C in the second heating curve. [b] Calculated in the range between 170 and 232 °C in the cooling curve.

Table 5. Composition, Titration, and MFR Data for Blends Obtained by Blending PA604 with PA6

blend	PA604 (wt %)	([NH$_2$]/ [COOH])$_0$[a]	[NH$_2$] (mequiv/kg)	[COOH] (mequiv/kg)	([NH$_2$]/ [COOH])[b]	M_n[c]	final torque (N m)	MFR (g/10 min)
PA601	0	1.02	27	29	0.93	19 600	0.6	32.6
PA-10	10	0.99	14.8	26	0.57	67 600	0.6	22.4
PA-25	25	0.95	12.8	24	0.53	78 100	0.8	18.1
PA-40	40	0.89	9.7	22	0.44	103 100	0.7	20.6
PA-65	65	0.76	10.7	25	0.42	93 500	0.6	27.6
PA-100	100	0.43	7.3	29	0.25	137 000	0.5	37.1

[a] Ratio between the starting concentration of $-NH_2$ and $-COOH$ groups. [b] Ratio between the final concentration of $-NH_2$ and $-COOH$ groups. [c] Calculated from $-NH_2$ concentration, neglecting possible thermooxidative reactions and assuming one $-NH_2$ per chain.

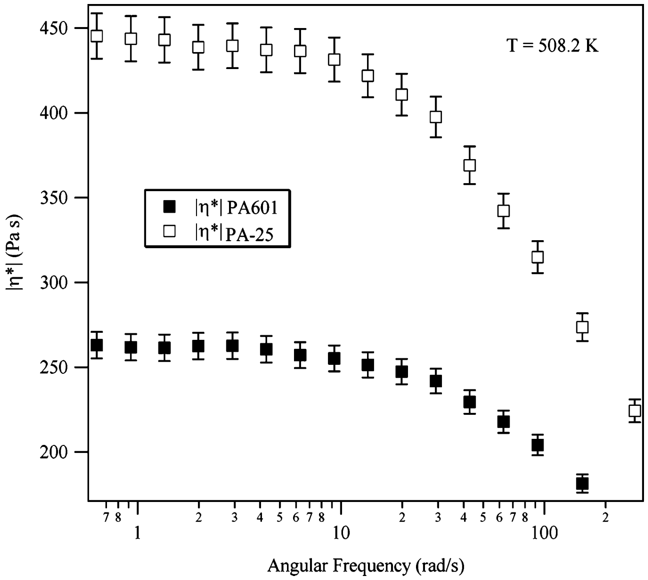


Figure 10. Complex viscosity as a function of angular frequency for polyamide 6 processed into a mixer (PA601) and for a mixture of polyamide 6 and PA604 (DEM functionalized polyamide 6) 75/25 by weight processed in identical conditions (PA-25).

the occurrence of shear thinning in both samples at the high-frequency side was observed.

Discussion

The final torque value (Table 1) of PA6 samples processed at 230 °C depends on the molar concentration of DCP and on the presence of unreacted liquid DEM in the melt acting as a plasticizer. In fact, the sample PA603 produced by adding only the peroxide showed the highest torque value, while PA604, which contains the greatest amount of DEM, showed the lowest one (Table 1). The FT-IR spectra of the acetone-extracted PA6 from the functionalization experiments were consistent with grafting of DEM on polyamide chains with formation of diethyl succinate (DES) groups. The presence of DES groups on polyamide macromolecules was confirmed by NMR, which allowed also the quantitative determination of functionalization degree (Table 1).

On the basis of titration results simply processed PA6 (PA601) showed a higher molecular weight than pure PA6 (PA6tq) (Table 3): this agrees with the condensation reaction between the end groups ($-NH_2$ and $-COOH$) in the melt at 230 °C.[37] A further remarkable decrease of [NH$_2$] is observed in the samples obtained by processing with DEM and peroxide. The data collected by titration analysis highlight that polyamide chains of functionalized samples had more $-COOH$ terminal groups than $-NH_2$ ones. This could be explained on the basis of the reaction of the terminal $-NH_2$ with the ester groups of DEM (Figure 11b) and grafted DES groups (Figure 11c) to give the corresponding imide. The latter reaction leads directly to branched PA6, while a similar branching can be obtained if the former reaction products graft to PA6 according to a free radical mechanism initiated by DCP (Figure 11d).

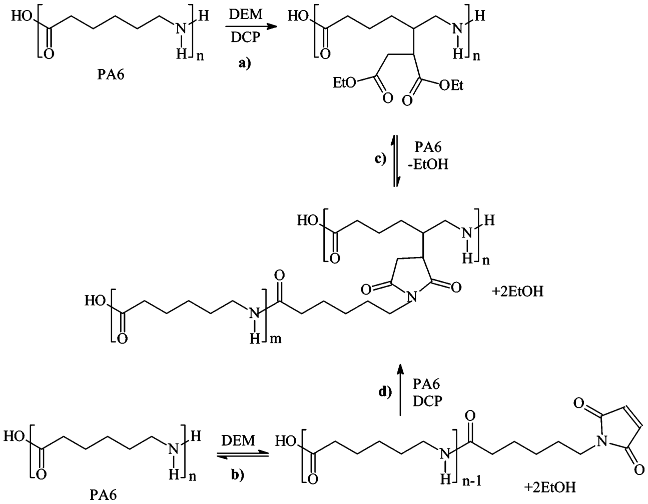


Figure 11. Possible mechanisms of $-NH_2$ consumption during the functionalization of polyamide 6 with DEM.

In the absence of peroxide (run PA605) the formation of terminal maleimide groups is confirmed by NMR analysis (Figure 7). In fact, the integral value of the protons on double bonds allows to calculate 0.39 mol % of maleimide end groups on the polyamide chain. By considering the titration results (Table 3), 0.32 mol % of maleimide terminals can be calculated, in agreement with the NMR value. In the presence of peroxide (PA604) unsaturated terminal groups could not be detected, thus supporting the hypothesis that the terminated maleimide chains undergo grafting (Figure 11d) to a very significant extent.

The equimolar disappearance of $-COOH$ and $-NH_2$ groups in the case of the not functionalized polyamides (runs PA601 and PA603) during the processing indicates an increase of molecular weight to longer linear chains by condensation of chain end groups independently of DCP. If one assumes that the same degree of chain extension takes places also for the grafted samples PA602 and PA604, the molecular weight of their chain, that is, of the linear fraction excluding the long PA6 branching, should be $M_n \approx 40\,000$ as for runs PA601. Since for the grafted PA6 a COOH/NH$_2$ ratio longer than 1 and no maleimide terminals were determined, the occurrence of branching can be hypothesized. The M_n values determined by titration for runs PA602 and PA604 assuming one NH$_2$ per chain resulted in $M_n = 90\,000$ and 110 000 g/mol, respectively. According to the COOH/NH$_2$ ratio, the two samples should contain an average of 0.7 and 1.3 long branching per macromolecules and then 1.7 and 2.3 carboxylic groups. This leads for the two samples to $M_n = 88\,000$ and 107 000, respectively, in good agreement with those calculated assuming one NH$_2$ per chain.

The total amount of grafted DES (Table 6) groups can be evaluated by summing those reacted $-NH_2$ groups (from

Table 6. Reacted and Free DES Groups Evaluation

sample	% reacted DES groups	% free DES groups	% reacted terminal NH_2 groups	BD[a] (branch/molecule)	FGGD[b] (DES/molecule)
PA602	2.5	97.5	42.1	0.7	32
PA604	3.1	96.9	57.1	1.3	48

[a] BD = branching degree calculated as number of long branched chains per macromolecule. [b] FGGD = free grafted groups degree calculated as number of free DES groups per macromolecule.

titration analysis) and those nonreacted (FD values from ^1H NMR). Although the ratio of grafted DEM to terminal NH_2 before grafting was more than ten, under our experimental conditions (high DEM/PA6) only about half of the end NH_2 groups reacted with DES groups. Despite the large DEM/$-NH_2$ molar ratio, this result is in agreement with previous data about DEM functionalized polyolefins and polyamide 6 reactive blending.[38]

The use of peroxide (PA603) leads to an increase in molecular weight due probably to chain extension, as confirmed by torque, melt flow rate (Table 1), and intrinsic viscosity results (Table 3). In the case of DEM and DCP modified samples the viscosity measurements agree with chain extension of polyamide and in particular with the structure of branched polyamides. However, the Huggins and Kraemer extrapolation should be used only for linear polymers; therefore, these results could be affected by a great uncertainty, derived also by the additional perturbation of the viscosimetric data induced by the presence of ester groups inserted onto the backbone.

With increasing the amount of long branches, the melting and crystallization temperatures as well as the corresponding overall transition enthalpy values decrease as for star-branched polyamides.[7] This is probably due to the defects introduced by grafting and chain branching onto the polyamide chains leading to shorter linear sequences and thus larger fractions of smaller sized and less regular lamellae. This effect is particularly evident in the SSA-DSC thermogram (Figure 9). The difference in the crystalline structure emphasized by the thermal fractionation is particularly striking in the high temperature range. In fact, the highest melting endotherm is partially suppressed in the case of PA602 and PA604, as a consequence of significant reduction of the polymer fraction characterized by longer linear sequences crystallized from the residual nuclei at Ts1 and melting at $T >$ Ts2 (Figure 1). The same polymer samples showed an increased crystalline fraction melting at $205 < T < 220$ °C, indicating that the structural changes occurred during the melt functionalization process did not disrupt dramatically their capability to crystallize. On the other hand, the increased polymer fraction melting in this intermediate temperature range for PA602 and PA604, characterized by larger molecular weights but viscosities comparable to the melt-processed PA601 and PA603, supports the hypothesis of a further increase of molecular weight due to branching rather than chain extension.

As the functionalized PA6 contains a large number of unreacted DES groups, the processing with pure PA6 was expected to produce an increase of the number of long branchings. By adding PA604 to the neat PA6, a further decrease of terminal $-NH_2$ concentration was observed ($[NH_2]$). The detectable difference between the theoretical value (dotted line in Figure 12) and the experimental one can be correlated directly to the occurring of the reaction of DES groups grafted on PA604 with NH_2 terminal groups of neat PA6. In fact, this difference decreases with PA604 content in the blend, that is, with terminal $-NH_2$ groups initial concentration decreasing, being the concentration of DES groups in excess for each composition.

Despite the apparent regular molecular weight increase obtained by titration, MFR showed a not monotonic decreasing trend as a function of PA604 concentration. The trend, showing a minimum point, can be fitted by a polynomial equation of fourth order. The composition corresponding to the minimum MFR value, as determined by finding the zero of the first-derivative function, was 25 wt % of PA604 (Figure 13). The disagreement between such trend of MFR data and $-NH_2$ concentration data, showing an increase of molecular weight with the increase of PA604 amount in the blend, can be tentatively explained by considering the behavior of melt volume rate (MVR) with time (Figure 14) for the various blends. At 235° MVR of the neat polyamide (PA601) increased with time during the test in agreement with the occurring of degradation. When 10 or 25% of PA604 was added, MVR decreases or remains unvaried as a function of time, thus indicating that branching reaction notably affects the rheological behavior. By further increasing the amount of PA604 MVR increased with time, thus suggesting the presence of competition between grafting and degradation.

Hence, on the whole the MFR results are affected by (1) the reactivity of PA604 in the blend with neat polyamide which produces an increase of molecular weight by the branching

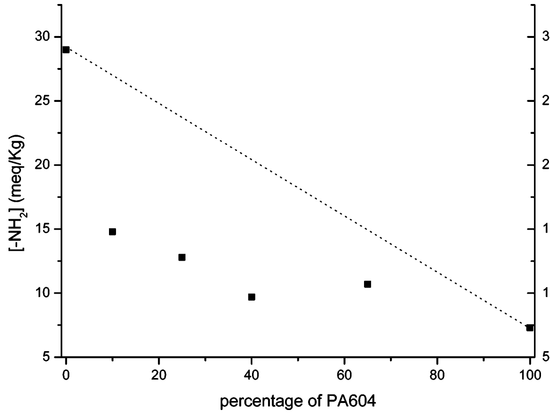


Figure 12. Terminal $-NH_2$ groups concentration against percentage of PA604 blended with neat PA6. The dotted line represents the theoretical trend, whereas black squares are referred to experimental results.

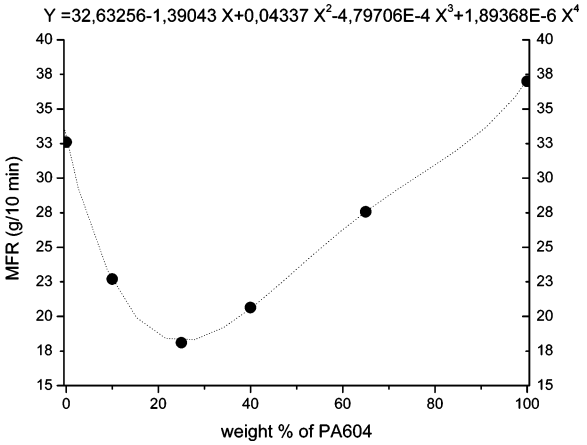


Figure 13. Melt flow rate against percentage of PA604 blended with neat PA6 and dotted fitting curve.

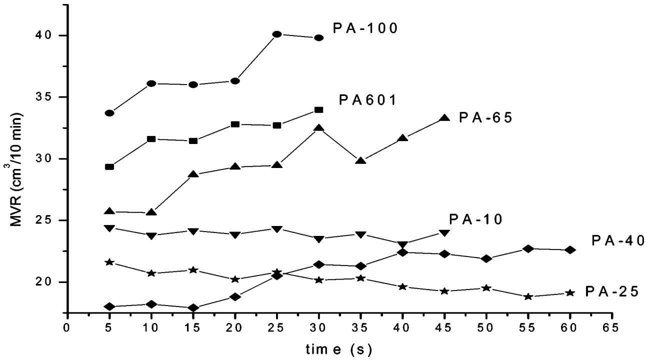


Figure 14. Melt volume rate against time for blends of PA604 and neat PA6.

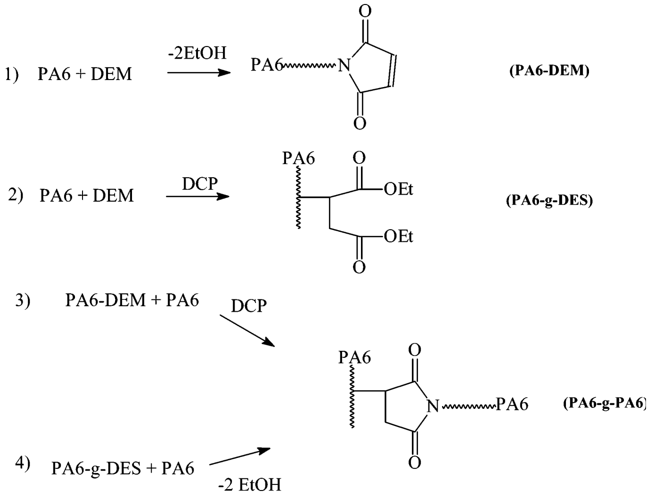


Figure 15. Reactions of PA6 and DEM in the presence of DCP in the melt (see also Figure 11).

reaction, (2) the degradation of both PA604 and PA6 during the MFR experiment, and (3) the more effective degradation that the modified polyamide undergoes during the blending with respect to neat polyamide probably due to the easier development in modified polyamide of thermooxidative reaction paths. This reaction cannot be detected on the basis of titration results and counterbalances the effect of the branching reaction, anyway occurring during blending, as confirmed by the depression of NH_2 concentration with respect to theorical values observed in Figure 14.

The comparison of the rheological properties of PA601 and PA-25 is in agreement with the previous MFR results, as the latter shows a higher viscosity than the former and the shear thinning effect is observed at lower frequency. Moreover, the shear thinning is more effective in the latter case, as shown by the complex viscosity drop (Figure 10). The differences between the two samples can be attributed to the simultaneous presence of a higher average molecular weight and long chain branches in PA-25, in agreement with Kolodka data about branched poly(propylene) obtained by copolymerizing propylene with poly(ethylene-*co*-propylene).[40] On the other hand, the presence of DES groups on the polyamide macromolecules should not influence the flow behavior, as short chain branches are reported to be not influent on rheological behavior of diethyl maleate grafted polyethylenes.[41]

Conclusions

The melt processing of polyamide in the presence of DCP and DEM produces short and long branching of the PA6 macromolecules. The process (Figure 15) involves the reaction between the polyamide chains and the monomer which produces a *N*-maleimide end groups polyamide (Figure 15, reaction 1), the free radical grafting onto the polyamide of the functionalizing agent (Figure 15, reaction 2), and the condensation reactions between the backbone grafted DES groups and the $-NH_2$ end groups of polyamide (Figure 15, reaction 4).

This last condensation reaction is not quantitative, and the amount of long branching is about one per PA6 chain. However, the branched polyamide obtained by this process shows thermal and rheological properties typical of star-branched polyamide synthesized by classical approaches.[5,9]

The branching reaction between DES groups and PA6 terminal groups is not complete due to the limited mobility of polyamide long macromolecules. However, the method offers a new and simple synthetic approach for branched and reactive polyamide macromolecules for a variety of applications. In particular, the possibility of attaining a higher viscosity by adding modified polyamide to neat one, reaching also an increased stability of viscosity as a function of time, proved successful, showing also the further reactivity of the DES grafted groups with the terminal amino groups of neat PA6 in a second blending step with consequent increase of the long branching grafting degree. Furthermore, the reported data provide a more detailed knowledge about the molecular complexity of the materials obtained by melt reactive processing of polyamides.

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