Macromol. Symp. **2004**, *218*, 51-60

Synthesis and Characterization of Star-Branched Nylon 12

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Summary: Linear and star-branched polyamide 12 were prepared in the presence of mono- and multifunctional acid agents. Molecular masses and molecular mass distributions are discussed according to our model recently presented and are compared with the data obtained by Flory's model. End group titration and SEC data are discussed. Oligomerisation data confirm the general validity of our model.

Keywords: equilibrium polycondensation; nylon 12; oligomerization; polyamide 12; star-branched polymers

Introduction

In the last years, an increasing interest has been present in the scientific and patent literature for polyamides having complex macromolecular architecture. Star-branched polymers are the simplest non linear polymers, characterised by a branch point from which emanate a number of polymer chains or "arms"; a consequence of this architecture is a reduction of their hydrodynamic volume respect to that of the corresponding linear macromolecules. The decreased molecular dimensions result in a lower viscosity both in solution and in the melt and allows for processing at lower temperatures and pressures as well as for processing higher molecular weight polymers. Moreover, reduced viscosity allows also for improved injection moulding[1,2,3]. These properties are important especially for high-melting polycondensation polymers. Both the physical properties of polymeric materials and their processing behaviour at high temperatures depend essentially on the average molecular weight and the molecular weight distribution (MWD). Star-branched polyamide 6 is now available for important technical applications[1]; as an example the material composed by Technylstar and fibreglass (50/50 by weight) presents an excellent surface aspect respect the analogous material prepared from linear nylon 6.

The first method of synthesis of pure star polymers is represented by the coupling reaction of living anionic polystyrene chains on silicon tetrachloride[4] but now star architectures can be produced with almost all polymerisation methods, and can be interpreted by two general schemes: 1) by terminating the reaction of linear polymers with a multisited reagent; 2) by initiating

DOI: 10.1002/masy.200451406

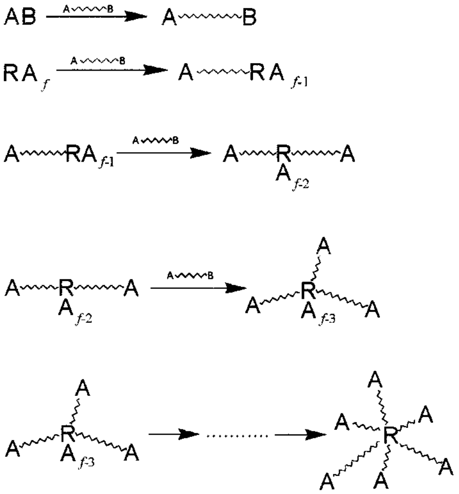
polymerisation from a polyfunctional agent. In the case of polycondensates, the termination reaction with a multisited agent can be performed also during the extrusion process while the second approach is performed by addition of the multifunctional agent during the polymerisation step. The two processes generally differ in the conversion of reacting groups.

Wilkes studied crystallisation behaviour[5] of star polyamide 6 prepared by using, as a comonomer, the second-generation starburst polyethyleneimine described by Tomalia[6]. Anionic polymerisation of caprolactam to give six-arms nylon 6 was studied by Mathias and Sikes[7,8]. Both these methods cannot be used in hydrolytic polymerisation conditions because of the low thermal stability of the comonomer[9] or to the poor control on the molecular mass distribution in caprolactam anionic polymerisation.

More important for the hydrolytic process are the theoretical and experimental results obtained by Flory[10,11] and Schulz[12], more than 50 years ago, in their studies about molecular weight distribution in polycondensation of AB type monomers with a polyfunctional agent RA_f (f is the functionality of active group A) at almost complete conversion. In these conditions, the molecular weight distribution becomes narrower increasing the functionality of the agent RA_f and the dispersion index D depends only on the functionality f, being $(1+1/f)$ at complete conversion[10]. The model proposed by Flory considers that a) in the polycondensation of AB type monomer with a polyfunctional agent RA_f there is a mixture composed solely of linear chains (derived from monomer AB) and of star-chains with f-arms; b) the length of the linear chains is equal to that of a branch of the star polymer (scheme 1). According to the same hypotheses, Farina[13] observed that during the polymerisation for $f > 2$ the dispersion index first increases, reaches a maximum and decreases until to the limiting value $(1+1/f)$. All these models were never tested in the industrial plant conditions in which functional group conversion is much lower than the one obtained in Flory's paper[11]. Also Feinauer's group used Flory model in order to explain their results[14-16]. Because of its industrial relevance, interest is generally devoted to star-branched nylon 6. In this paper we discuss synthetic and analytical results for star-branched nylon 12 according to our recently presented model[17] which was applied to Rhodia industrial process for Thecnylstar[1]. The presence of the star structure was demonstrated also by oligomerisation[18]. Our data are compared to data evaluated according to Flory's model.

Theoretical aspect

For star polycondensated polymers we presented a new model able to describe the final composition when multifunctional agents are used in the hydrolytic polycondensation of A-B monomers[17]. Scheme 1 reports the reactions related to the growth of macromolecular chains of the AB monomer in the presence of a multifunctional reagent RA_f and allows a better understanding of the two models.



Scheme 1. Reaction scheme between the RA_f and AB monomer.

According to this scheme and under the hypothesis of the independent and equal reactivity of the functional groups from the molecular mass, our model relates molecular mass data to the initial feed and to conversion of functional groups. We here report only the final equations for the molecular parameters as function of the concentrations of terminal groups; in the paper we will refer to a multifunctional agent RA_f where A = COOH and B = NH_2.

In general, each property of the polymer depends on the ratio between star-branched and linear species and as a consequence, it is important to measure or estimate the mole fraction of the total star polymer (f_S) *vs* the linear one (f_L) in order to reach a rational balance in the final properties.

Equations 1 and 2 allow this measure starting from initial feed and end-groups titration:

$$f_S = 1 - f_L \tag{1}$$

$$f_L = \left\{[NH_2] + \frac{fC_0(N_0 - [NH_2])}{[COOH]}\left(\frac{[COOH]}{N_0 + fC_0}\right)^f\right\} \Big/ \left\{[NH_2] + C_0\left(1 - \left(\frac{[COOH]}{N_0 + fC_0}\right)^f\right)\right\} \tag{2}$$

where C_0 and N_0 are the initial concentrations of polyfunctional agent RA_f (with f functionality) and monomer AB, $[NH_2]$ and [COOH] are the mole concentrations of terminal groups. In the same way molecular mass data can be obtained from equations 3-5.

$$\overline{DP_n} = \frac{N_0}{[NH_2] + C_0\left(1 - \left(\frac{[COOH]}{N_0 + fC_0}\right)^f\right)} \tag{3}$$

$$\overline{DP_w} = \frac{2N_0 + fC_0 - [NH_2]}{[COOH]} + \frac{C_0}{N_0} f(f-1)\left(\frac{N_0 - [NH_2]}{[COOH]}\right)^2 \tag{4}$$

$$D = \frac{\overline{DP_w}}{\overline{DP_n}} \tag{5}$$

$$[COOH] = [NH_2] + fC_0 \tag{6}$$

When reaction goes to completion (i.e. $[NH_2] = 0$), the limiting values of number- and weight-average degree of polymerisation and dispersion index can be evaluated[17]. From the equations reported, concentration of all species and molecular mass distribution can be evaluated from the initial feed and end-group determination at each polymerization stage.

Experimental part

Polymerisations were performed in a home-made stainless steel reactor; laurolactam (LL) (Aldrich, purity >98%) hydrolysis was obtained in the presence of an excess of water (W/LL=1.2) and of the multifunctional reagent; phosphoric acid (Aldrich, purity > 98%) (15-20 ppm) was added as catalyst. As mono, tri- and tetra-functional agents benzoic acid (Aldrich, purity > 99,5%), trimesic acid (Aldrich, purity > 95%) and 2,2,6,6-tetra(β-carboxyethyl)cyclohexanone (synthesised according to literature[19]) were used. Reactions were performed at 270°C. A pressure of 35 Bar was measured at the beginning of the reactions; after 4 hours the reactor was cooled, the excess pressure eliminated and polycondensations continued at 270°C under a nitrogen flow.

The titration of amino end groups in the polyamides was carried out by potentiometer Metrohm 751 GPD Titrino; polyamide (3-4% by weight) was dissolved in m-cresol/methanol mixed solvent (85/15 V/V) and was titrated by HCl N/100 in methanol.

SEC analyses were performed in anhydrous CH_2Cl_2 at room temperature using a six Ultrastyragel column set (10^5, $2*10^4$, $2*10^3$ and 500 Å) and a UV detector operating at 244 nm. Molecular masses of the polyamides were determined after N-trifluroacetylation reaction[20]. Column calibration was performed by polystyrene standards; the linear polyamide calibration curve was calculated according to the universal calibration principle[21,22].

NMR spectra were run in CF_3COOD solution with a Bruker 400 MHz spectrometer.

Results and discussion

The initial feeds for the synthesis of linear or star nylon 12 are reported in table 1. In the optimised experimental conditions, the conversion of the cyclic monomer is almost complete as demonstrated by SEC analysis.

Table 1. Feed(*), titration and molecular mass data of prepared samples.

Sample	f	Molar % C_0/N_0	NH_2	Mn		Mw		D		weight fraction % (linear species)	
			meq/Kg	a	b(**)	a	b	a	b	a	b
1	1	0,125	28,48	28741	28734	57204	57432	1,99	2,00	100	100
2	1	0,250	29,74	23600	23599	46993	47140	1,99	2,00	100	100
3	1	0,500	19,11	22537	22588	44961	44973	1,99	1,99	100	100
4	3	0,125	25,37	31675	31814	64439	69975	2,03	2,04	58,86	58,03
5	3	0,250	19,25	31635	31872	58804	59310	1,86	1,86	36,01	34,45
6	3	0,500	9,38	29371	29758	45382	45902	1,54	1,54	14,33	11,39
7	4	0,125	17,92	41047	41544	85813	87559	2,09	2,11	41,77	41,51
8	4	0,250	17,13	33440	34075	62251	63582	1,86	1,87	25,61	25,38
9	4	0,500	10,54	27759	28738	42097	43550	1,52	1,51	9,80	9,52
10	1	20,0	-	-	-	-	-	-	-	-	-
11	1	50,0	-	-	-	-	-	-	-	-	-
12	3	11,1	4,88	1837	2285	2618	3119	1.43	1,36	43.27	0,36
13	3	33,3	10,40	688	1080	1004	1488	1,46	1,38	74,44	0,33
14	4	25,0	75,40	793	1944	1136	2651	1,43	1,36	52,54	2,09
15	-	-	32,25	30987	31008	61620	62016	1,99	2,00	100	100

(*) LL quantity in each sample is 50g.

(**) *a* and *b* refer to our and Flory model

In a previous paper we used the oligomerisation of AB monomers in the presence of polyfunctional agent, in order to verify the thermal stability of the multifunctional agent in the polymerisation conditions and the validity of the model proposed[18]. Table 2 presents evaluated and 1H NMR data for the sample 12 and 13; in this case trimesic acid (RA_3) was used as multifunctional agent. The agreement between experimental data and the data evaluated according to our model is excellent.

In figure 1 we compare SEC curves of the reference sample 15 and of a linear nylon 6. In these analytical conditions the peak of the cyclic monomer appears at about 60 min and elutes at about the same time of the multifunctional reagent; the highest cyclic monomer concentration was observed in sample 15.

Table 2. 1H NMR and evaluated data of oligomeric mixture obtained in the presence of a trifunctional agent.

Sample	Method	RA_3	$RA_2(NHR)_1$	$RA_1(NHR)_2$	$RA_0(NHR)_3$
12	Model	0.0147	0.1361	0.4191	0.4301
	NMR	0.0140	0.1420	0.4208	0.4232
13	Model	0.1201	0.3700	0.3799	0.1300
	NMR	0.1265	0.3619	0.3689	0.1427

From figure 1, the different contribution of cyclic oligomeric species to the final polymer compositions can be measured in the two polymers. As a consequence of the lower concentration of cyclic species in nylon 12, there is a better correspondence between the theoretical distribution and experimental SEC curve for linear nylon 12 respect to the corresponding nylon 6.

Moreover, according to the growing scheme of the macromolecular chains for AB monomers in the presence of polyfunctional agents, no crosslink was observed in the SEC analyses.

The effect of the multifunctional agent concentration on molecular mass distribution is reported in figure 2; as expected from the model, the average numerical mass and hydrodynamic volume decrease by increasing the concentration of the multifunctional agent.

The effect of functionality (f value) is clearly observed in figure 3; SEC curves refer to samples prepared in the presence of mono-, tri- and tetrafunctional agent at the same molar concentration. The different widths of the curves correspond to the expected theoretical distributions.

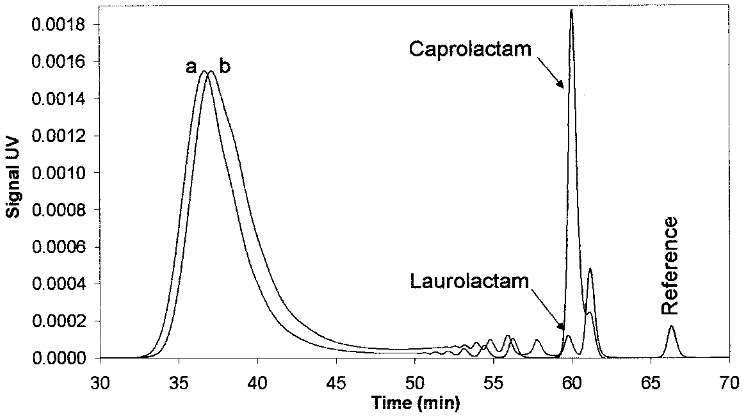


Figure 1. SEC curves of sample 15 and of a linear polyamide 6.

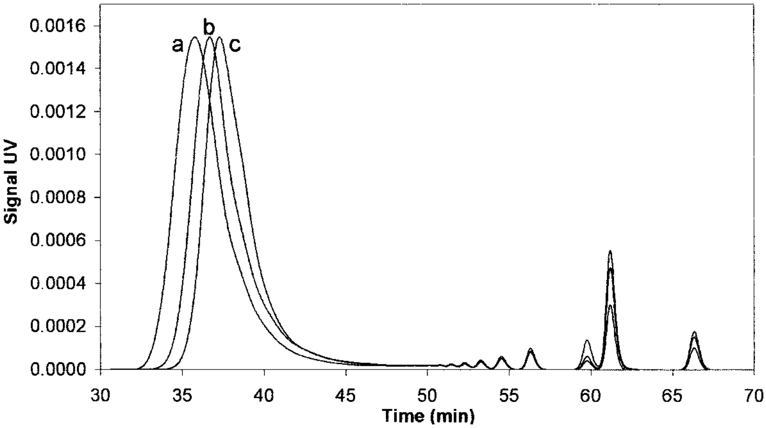


Figure 2. a) Sample 7; b) Sample 8; c) Sample 9.

In order to test the correspondence between analytical data and the mass evaluated from the model, two different problems have to be solved: the first one is related to end-group determination in nylon 12 and the second one to the calibration of the GPC column set.

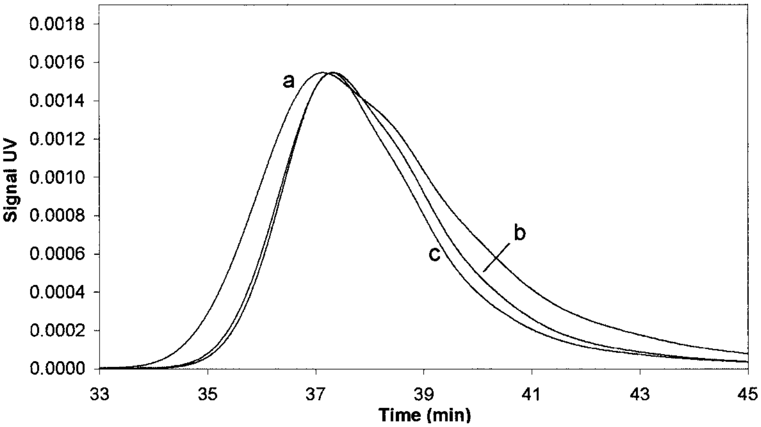


Figure 3. a) Sample 3; b) Sample 6; c) Sample 9.

An excellent titration methodology is well known for Nylon 6 or 66: the polymer is soluble in trifluoroethanol and can be titrated by usual water standard acidic or basic solutions. Polymers with longer hydrocarbon chain cannot be dissolved in this solvent and more complicated procedures must be used. The titration procedure used in this work derives from that used by Wolf and Möbus [23] but allows a better quantitative determination of amino end groups; the measure of acidic end groups suffers for the solvent acidity and of the initial unbalance between amino and acidic functions. However in order to test our models it is sufficient the knowledge of the initial feed and of amino end groups. Both polyamide 12 and polyamide 6 completely dissolve in the solvent mixture used. A standard linear polyamide 6 (DP_n = 160) was titrated both with trifluoroethanol and the m-cresol/methanol mixture; an excellent agreement between the data obtained was found.

In table 1, we also report amino end group concentration and molecular mass values calculated according to the two models.

In this table, the concentration of carboxy end groups is not reported, but it can be easily calculated from the initial concentration of the polyfunctional agent and of the amino end groups according to equation 6.

A comparison between the two models can be done from data in table 1; the two models give equivalent results for linear polymers (Samples 1-3 and 15). The concentration of linear species is higher when evaluated with our model as it takes into account all the possible linear macromolecules (Samples 4-9) and the difference in linear species concentration increases by increasing commoner concentration (Samples 4-6, 7-9). Our model is able to predict molecular composition even at high comonomer concentration (Samples 12-14, table 2).

In table 3 we report molecular mass data obtained from SEC curves. Data are reported as linear polyamide 6 equivalent; in the case of linear polyamide 6, the validity of universal calibration concept was demonstrated for SEC analyses of N-trifluoroacetylated polymers[20,21]. It is important to note that the use of a polystyrene calibration in the evaluation of SEC curves can give very different molecular mass data; as an example M_n = 79440, M_w = 147700, M_z = 236250, D = 1.86 and D_z (M_z/M_w) = 1.60 were evaluated for the sample 15.

Table 3. Molecular mass data obtained with a calibration for linear polyamide 6.

Sample	Mn	Mw	Mz	D	Dz
1	29544	60748	96701	2,01	1,63
2	24788	49339	79298	1,99	1,61
3	22661	44604	71375	1,97	1,60
4	30338	55752	92743	1,84	1,66
5	29657	51535	86170	1,74	1,67
6	26958	42139	60698	1,56	1,44
7	48139	93996	148334	1,95	1,58
8	32502	57623	84227	1,77	1,46
9	28074	42672	57366	1,52	1,34
15	31913	63232	103255	1,98	1,63

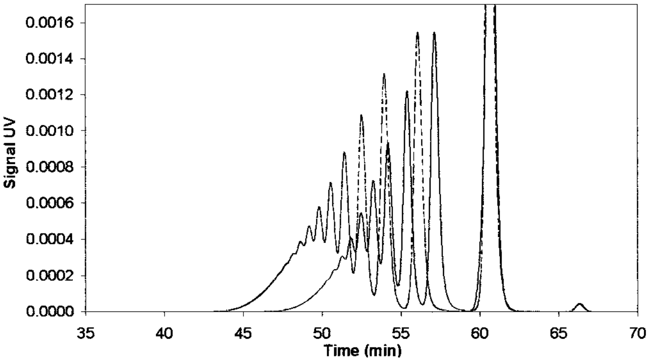


Figure 4. SEC curves of linear oligomeric mixtures obtained from lauro- (---) and caprolactam (—) in the presence of benzoic acid.

Figure 4 shows SEC curves of linear oligomers of lauro- and caprolactam obtained using benzoic acid as mono-functional agent. A specific calibration curve derived from linear oligomers of caprolactam was first used to calculate the molecular masses of laurolactam oligomers but a systematic error occurred (3-5% by molecular mass): this error at a first sight might be considered acceptable, but it indicates that a more accurate calibration curve should be used.

In order to get a better curve, MALDI-TOF and SEC analyses should be used at the same time.

Acknowledgments

Authors acknowledge INSTM (Consorzio Interuniversitario di Scienza e Tecnologia dei Materiali) for partial financial contribution and Cesare Guaita and Franco Speroni (Rhodia Engineering Plastics) for useful discussions.

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