

COMPOSITION AND RHEOLOGY OF POLYAMIDE-6 OBTAINED BY USING BI- AND TRI-FUNCTIONAL COUPLING AGENTS

J.J.M. Slot^{a,b,*}, E. van Ruymbeke^a and P.A.M. Steeman^a

^a Materials Science Centre, DSM Research, Geleen, The Netherlands

^b Department of Mathematics and Computer Science, Eindhoven University of Technology, Eindhoven, The Netherlands

Abstract A statistical approach is developed, based on a Monte Carlo method, in order to determine the statistical composition of a polyamide-6 sample composed of caprolactam (an AB-type monomer) and of a di-acid (A_2 type) or a tri-acid (A_3 type) as coupling agents. For this composition, the linear rheological behavior of these systems is predicted using a tube-based theory. This allows us to show that while coupling agents of type A_2 can be seen as flow improver, the effect of branching agents of type A_3 , depending on the synthesis recipe and the conversion level, can lead either to an increase or to a decrease of the viscosity. By adding specific amount of these agents, we also show that it is possible to obtain materials with the same zero-shear viscosity but with different shear thinning behavior. Furthermore, the polydispersity of linear samples of the same average number molecular weight, M_n , is discussed in function of the amount of A_2 monomers they contain. Ranging from 2 to 1.5, this difference in polydispersity is expected to have a significant influence on the processing behavior of such materials.

Keywords: Polyamide-6; Random branching; Statistical composition; Rheology; Monte Carlo; Tube theory.

INTRODUCTION

In the case of industrially synthesized polycondensates such as polyamide-6 (PA6), very limited routes are available to produce well-designed polymeric chain architectures because of the intrinsic random nature of the polycondensation process^[1, 2]. In particular, linear PA6 samples will typically show a molecular weight distribution (MWD) which is well approximated by a Flory distribution, characterized by a polydispersity (PDI) around 2^[3–8]. Therefore, since the processing and rheological properties strongly depend on the sample composition and MWD, it is not straightforward to modify the shear thinning behavior of a linear PA6 while keeping a similar average molecular weight. In order to overcome this issue, it has been shown that introducing random branching *via* the addition of multi-functional agents to the reaction mixture is a good way to enhance the variety in flow behavior of these samples^[1, 6–10]. This also allows one to obtain a better balance between processability and mechanical properties of the final solid material^[11–13].

The objective of this work is to model and discuss the influence of adding bi- and tri-acid-functional monomers in a linear PA6 on its composition and MWD and on its rheological behavior. It is expected that the presence of bi- and tri-functional monomers will lead to a certain amount of two arm and three arm star molecules. It must be noted here that while the two arm star chains are in fact linear, they still need to be distinguished from the linear chains obtained without any coupling agent since they have an average number molecular weight twice as large as these ordinary linear molecules^[14].

* Corresponding author: J.J.M. Slot, E-mail: han.slot@dsm.com

Invited lecture presented at the International Symposium on Polymer Physics, 2012, Chengdu, China

Received September 24, 2012; Revised October 9, 2012; Accepted October 10, 2012

doi: 10.1007/s10118-013-1214-y

In the literature, it has been shown that adding bi- and tri-functional coupling agents can lead to a significantly lower viscosity in the melt and in solution^[9, 10]. These additives are therefore seen as flow improvers or plasticizing agents. However, their effect is strongly dependent on the initial recipe and on the conversion level of the reaction. In specific cases, an increase of the zero-shear viscosity can even be observed. Furthermore, the viscoelastic properties of the PA6 might or might not be strongly influenced by the functionality of the coupling agent (bi- versus tri-functional), again depending on the initial recipe. The objective of this work is to investigate these different trends in a systematic way and to propose a clear picture of the different processes, sometimes having opposite effects, that influence the flow properties of PA6 systems in the presence of di- or tri-functional coupling agents.

In order to do so, first a statistical approach is developed and validated, which links the reaction recipe to the sample composition. This allows us to discuss the evolution of the architecture and molecular weight of the chains. Then, based on a mesoscopic, tube-based model, the related viscoelastic behavior of these samples is predicted in order to discuss the influence of the sample composition on its rheology. Results are discussed for different recipes, with different amounts and lengths of linear and star molecules. In the last section, conclusions are presented.

MODELING CONSIDERATIONS

Sample Composition

The sample composition is determined, based on a Monte Carlo approach^[3-5]. In particular, the following assumptions are made: (1) an A-group reacts only with a B-group and vice versa; (2) all reactions have equal probability; (3) no intra-molecular reactions occur, *i.e.* no cycles are formed. Based on these assumptions, adding bi- or tri-functional coupling agents to a linear PA6 sample can only lead to a mixture of linear, “double linear” (or two arm star) and three arm star molecules. Indeed, since the caprolactam is a monomer of type “AB” (A = acid group, B = amino group) and the bi- and tri-acids are of type “A₂” and “A₃” respectively, the extremities of the arms attached to these A₂ and A₃ monomers will necessarily be of type “A”. Therefore, it is not possible to obtain a chain containing more than one coupling agent (and thus more than one branching point).

Since A₂ or A₃ monomers are added, the final composition of the sample will contain an excess of acid groups. Therefore, at full conversion, it is expected that all the chain extremities are of type “A”. However, at lower conversion level of the A groups, p_A , some of the B groups did not react yet. Their number is defined such that:

$$p_A = \frac{\text{reacted B}}{\text{total A}} \quad (1)$$

In order to account for these non-reacted B groups, we consider here that they reacted with virtual A end-groups, called A₁'. Thus, an AB-AB-...-AB chain, which has an extremity of type B rather than of type A, is considered as a AB-AB-...-AB-A₁' chain. With such a picture, the conversion level p_A is equal to:

$$p_A = \frac{\text{reacted B}}{\text{total A}} = \frac{N_{AB}}{3N_{A_3} + 2N_{A_2} + N_{A_1'} + N_{AB}} \quad (2)$$

with N_{AB} the number of AB groups *etc.* Every chain can be considered as “closed” by only A groups, even at low conversion level. The number of virtual end groups A₁' is thus determined on the basis of Eq. (2).

As already mentioned, the possible architectures that can be obtained in the sample by adding bi- and tri-functional agents in caprolactam are linear, double-linear and star chains. These different architectures are represented in the cartoon in Fig. 1.

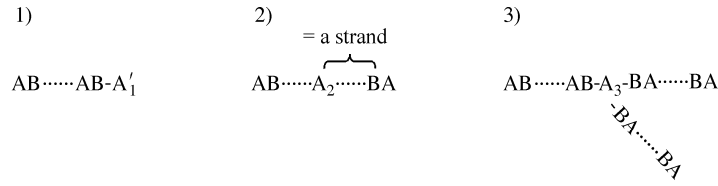


Fig. 1 Cartoon of the possible architectures obtained by adding the coupling agents A_2 and A_3 to caprolactam AB

Since the PA6 is a polycondensation polymer, its composition can be described by Flory statistics^[1, 3–6]. In particular, it is known that every AB-AB-...AB strand of any molecule has the same average number molecular weight, called $M_{n, \text{strand}}$ ^[6–8]. Furthermore the MWD of these strands will follow a Flory distribution. Since every A_2 (A_3) monomer will generate two (three) strands and since every A_1' will generate one strand, the total number of strands in a sample, $\#_{\text{strands}}$, can directly be obtained from the synthesis recipe:

$$\#_{\text{strands}} = 3N_{A_3} + 2N_{A_2} + N_{A_1'} \quad (3)$$

Knowing the total number of strands, the number-average molecular weight of these strands can then be determined from the total amount of AB, A_2 and A_3 monomers in the sample:

$$M_{n, \text{strand}} = \frac{M_{\text{total}}}{\#_{\text{strands}}} = \frac{N_{A_3} m_{w, A_3} + N_{A_2} m_{w, A_2} + N_{AB} m_{w, AB}}{\#_{\text{strands}}} \quad (4)$$

In which m_{w, A_x} , $m_{w, AB}$ represent the weight of the corresponding monomers (such as for caprolactam, $m_{w, AB} = 113.16$ g/mol).

In order to determine the sample composition, we also need to calculate the weight proportion of linear, double-linear or star molecules. These values are also directly found from the synthesis recipe. Indeed, since — in average — every strand has the same molecular weight, φ_{lin} , $\varphi_{\text{double-lin}}$ and φ_{star} become:

$$\varphi_{\text{lin}} = \frac{N_{A_1'}}{N_{A_1'} + 2N_{A_2} + 3N_{A_3}} \quad (5)$$

$$\varphi_{\text{double-lin}} = \frac{2N_{A_2}}{N_{A_1'} + 2N_{A_2} + 3N_{A_3}} \quad (6)$$

$$\varphi_{\text{star}} = \frac{3N_{A_3}}{N_{A_1'} + 2N_{A_2} + 3N_{A_3}} \quad (7)$$

Based on Eqs. (4) to (7), the overall MWD can then be determined. To do so, we first determine the MWD corresponding to the double-linear chains and to the star chains (note that the MWD of the linear chains is known since it is a Flory distribution with $M_n = M_{n, \text{strand}}$). To this end, we apply the same procedure as developed in Ref. [15], based on the fact that association between two strands of mass M_i and M_j will be proportional to the product of the number fractions of these strands.

In order to build the distribution for each architecture, the MWD of the linear parent polymer is split into 20 different intervals (bins) having an average molecular weight M_i and a weight fraction ω_i . Then, all possible combinations are taken into account. At this stage, molecules with the same arms but taken in a different order (as, for example, the M1-M2-M3 3-arm star compared to the M1-M3-M2 3-arm star), are considered different. In order to determine the probability of having, for example, a specific 3-arm star molecule, its number probability, $p_{\#}(M_i, M_j, M_k)$, is first calculated from the number probability, $p_{\#, b}$, of each kind of arm:

$$p_{\#,j} = \frac{\left(\frac{\omega_i / \sum_k \omega_k}{M_i} \right)}{\sum_k \left(\frac{\omega_k / \sum_n \omega_n}{M_k} \right)} \quad (8)$$

$$p_{\#}(M_i, M_j, M_k) = p_{\#,i} p_{\#,j} p_{\#,k} \quad (9)$$

Indeed, since the probability of a linear chain to be included in the formation of a star molecule depends only on the living chain end and not on its length, the weight probabilities cannot be used at this level of the calculations. However, the linear viscoelasticity of a polymer depends on the weight fraction of each kind of molecules. The weight probability, $p_{\omega}(M_i, M_j, M_k)$, is determined from $p_{\#}(M_i, M_j, M_k)$ as follows:

$$p_{\omega}(M_i, M_j, M_k) = \frac{p_{\#}(M_i, M_j, M_k) \cdot (M_i + M_j + M_k)}{\sum_{l,m,n} p_{\#}(M_l, M_m, M_n) \cdot (M_l + M_m + M_n)} \quad (10)$$

From $p_{\omega}(M_i, M_j, M_k)$, the weight fraction of each branch of this specific star molecule is then determined from:

$$p_{\omega}(M_i \text{ in } (M_i, M_j, M_k)) = p_{\omega}(M_i, M_j, M_k) \cdot \frac{M_i}{(M_i + M_j + M_k)} \quad (11)$$

Then, all the star molecules having the same three arms but in a different order, are considered together and their corresponding volumetric fractions are added. The same procedure is used for the double linear. This algorithm has been validated in Ref. [15].

As a representative example, the MWD of the linear chains, the double linear chains and the 3-arm star polymers obtained by using Eqs. (8) to (11) and assuming that the MWD of the linear chains are Flory distributed are shown in Fig. 2. The distributions have been normalized such as:

$$\int_{-\infty}^{+\infty} \frac{dw(\lg(M))}{d \lg(M)} d \lg(M) = 1 \quad (12)$$

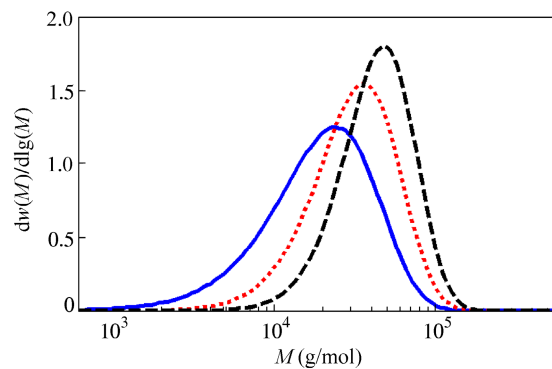


Fig. 2 Flory distribution of a strand with $M_{n, \text{strand}} = 12 \text{ kg/mol}$ (—) and MWD obtained from the association of two (···) or three (- -) of these strands

As expected, the MWD resulting from the association of n strands, *i.e.* of n Flory distributions of mass $M_{n,\text{strand}}$ leads to a distribution with a number-average molecular weight of $M_n = n M_{n,\text{strand}}$ and an weight-average molecular weight of $M_w = (1 + 1/n) M_n$.

The final MWD is then obtained by combining these three MWDs corresponding to the linear, the double-linear and the star chains, in the right proportions (see Eqs. (5) to (7))^[15, 16].

In this way, based on the recipe, the sample composition as well as all the necessary information to predict its rheological behavior is known.

Modeling the Linear Viscoelasticity (LVE) of Polydisperse Linear/Star Blends

Stress relaxation function $G(t)$

In order to predict the LVE of the blends, we use the time-marching algorithm developed in previous works for predicting the LVE of linear^[17], star^[18], H, pom-pom^[19] and tree-like^[20] polymers. This tube-based model expresses the stress relaxation function $G(t)$ of the polymer at time t by taking into account both the high frequency-Rouse relaxation of the polymer and the disentanglement relaxation function $G_d(t)$, which includes a classical description of reptation, contour length fluctuations, and constraint release processes^[15]:

$$G(t) = G_d(t) + \sum_i \varphi_i \left(\frac{\rho RT}{M_i} \sum_{p=Z_i+1}^n \exp\left(\frac{-p^2 t}{\tau_R(M_i)}\right) + \frac{1}{4} \frac{\rho RT}{M_i} \sum_{p=1}^{Z_i} \exp\left(\frac{-p^2 t}{\tau_R(M_i)}\right) \right)$$

$$G_d(t) = G_N^0 \left(\sum_i \varphi_{\text{linear},i} \int_0^1 p_{\text{rept}}(x_{\text{lin}}, t) p_{\text{fluc}}(x_{\text{lin}}, t) dx_{\text{lin}} + \sum_i \varphi_{\text{star},i} \int_0^1 p_{\text{fluc}}(x_{\text{star}}, t) dx_{\text{star}} \right)^{\alpha+1} \quad (13.a)$$

where G_N^0 is the plateau modulus, $\varphi_{\text{linear},i}$ and $\varphi_{\text{star},i}$ are the weight fractions of the different linear chains (including both the linear and the “double linear” chains) and star branches in the polymer, ρ is the polymer density, T is the temperature and $\tau_R(M_i)$ is the Rouse relaxation time of a chain of mass M_i and proportion φ_i . Furthermore $p_{\text{rept}}(x, t)$ and $p_{\text{fluc}}(x, t)$ are the survival probabilities of the initial tube segments localized at the normalized position x (going from 0 at the chain extremity to 1, at the middle) at time t , for the reptation and contour length fluctuations processes, respectively. The $(\alpha + 1)$ exponent takes into account the dynamic tube dilution process, with the dilution exponent α being fixed to 1^[21]. By summing up these survival probabilities along all the chains according to their proportion at time t , the total unrelaxed fraction of the polymer at this specific time is then obtained.

As explained in details in Ref. [15, 18], the survival probabilities $p_{\text{rept}}(x, t)$ and $p_{\text{fluc}}(x, t)$ can be described by time-decreasing exponential functions depending, respectively, on the reptation and fluctuations times of the different molecular segments along the chains. Thereby taking into account the polymer fraction that is already relaxed in the form of solvent speeding-up the relaxation of the remaining initial tube segments^[22, 23].

On the other hand, the relaxation of unentangled molecules of mass M_k is only described by the high frequency-Rouse process. In such a case, their contribution $G_k(t)$ to the stress relaxation function $G(t)$ is:

$$G_k(t) = \varphi_k \left(\frac{\rho RT}{M_k} \sum_{p=1}^n \exp\left(\frac{-p^2 t}{\tau_R(M_k)}\right) \right) \quad (13.b)$$

Finally, from the relaxation function $G(t)$, the storage and loss moduli are determined using the Schwarzl functions^[24].

Material parameters

The material parameters required in order to predict the linear viscoelasticity of a polymer melt are the plateau modulus, the average molecular weight between two entanglements and the Rouse time of an entanglement segment. For PA6, these parameters have been fixed, based on experimental data at 260°C^[1], and are given by

1.8 MPa, 2000 g/mol and 1.9×10^{-7} s, respectively.

RESULTS AND DISCUSSION

Adding A_2 Bi-functional Coupling Agents in Caprolactam AB Monomers

Influence of the conversion level p_A

We first look at the composition of a sample which contains a fixed amount of A_2 coupling agents and caprolactam (AB), at various conversion levels. As shown in Fig. 3, the conversion level must be close to the full conversion level in order to obtain a significant proportion of double-linear chains (*i.e.* containing a A_2 monomer). Indeed, as described by Eqs. (5) and (6), the proportion of linear chains directly depends on the number of virtual A_1' end-groups, which increases at low conversion levels (see Eq. (2)).

At full conversion (of the B groups), *i.e.* for $p_A = 0.9901$ in the specific case proposed here (with 3 A_2 for 600 AB), all the chains are double-linear chains and the polydispersity of the sample decreases from 2 (for 100% linear chains) to 1.5 (see Fig. 3b). Increasing the conversion level also leads to larger average molecular weight of the material and of the strand. This is expected since the chains have a smaller probability to stop growing.

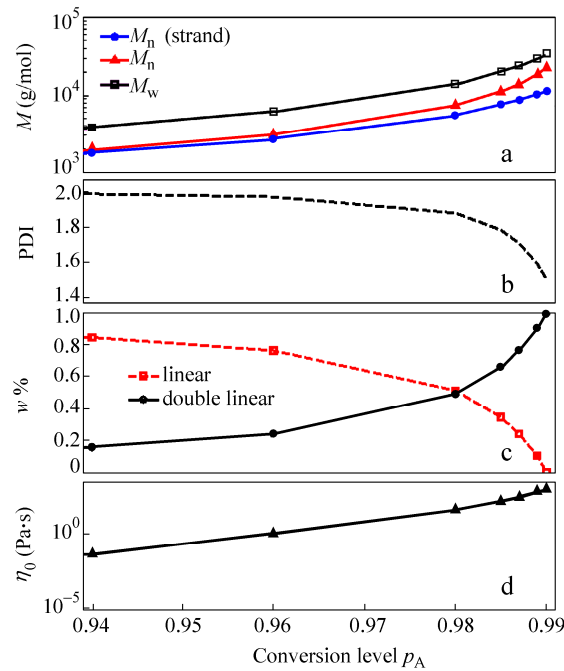


Fig. 3 Viscosity and composition of a sample containing 600 AB and 3 A_2 , at different conversion levels p_A (from $p_A = 0.94$ to $p_A = 0.9901$): (a) average molecular weight in number and in weight of the sample and $M_{n, \text{strand}}$, (b) polydispersity (PDI), (c) weight proportion of linear and double linear chains and (d) evolution of the zero-shear viscosity η_0 .

Since the weight-average molecular weight of the sample, M_w , increases with p_A , we consequently observe an increase of the zero-shear viscosity, see Fig. 3(d). As illustrated in Fig. 4, this is due to the increasing terminal relaxation time of the linear chains, scaling with $M_w^{3.4[25-27]}$. It must be noted that for a conversion level equal or lower than 0.96, the theoretical storage modulus does not show any plateau: chains are not or only poorly entangled.

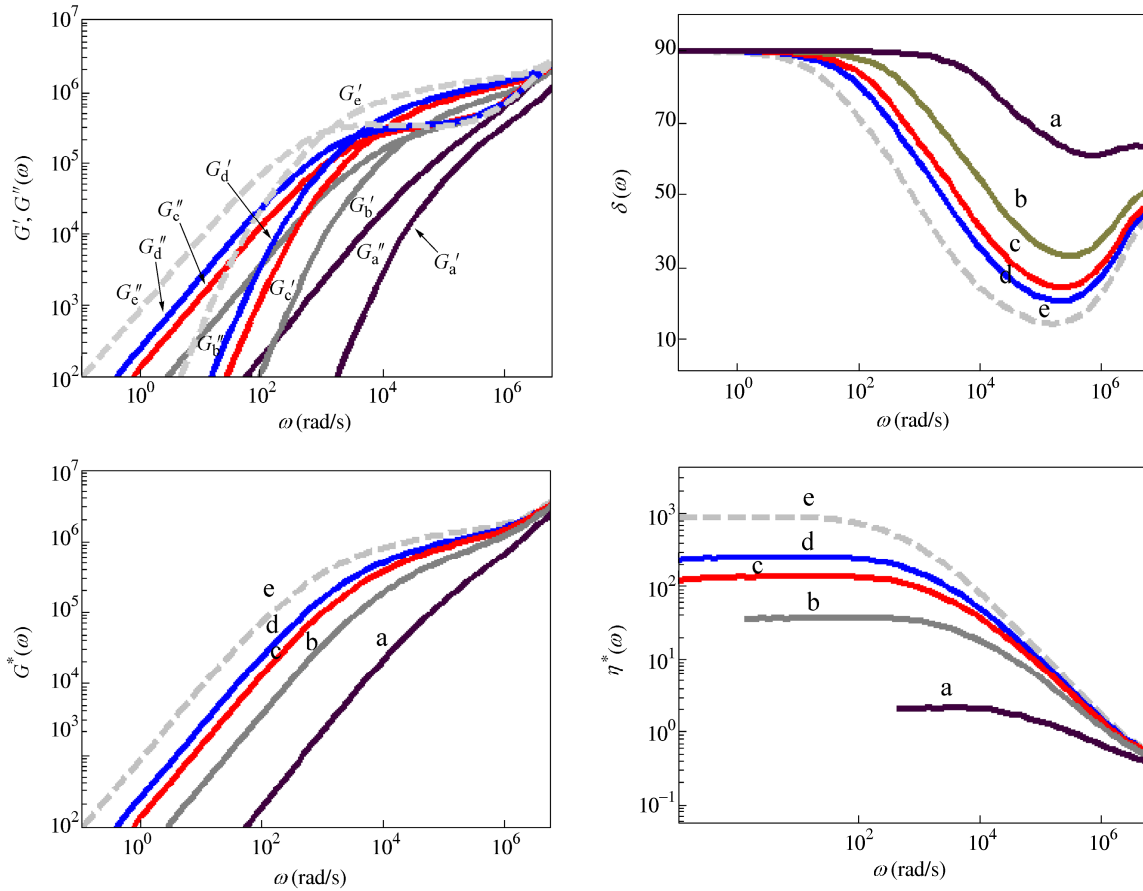


Fig. 4 Linear viscoelastic curves predicted based on sample compositions described in Fig. 3, with $p_A = 0.96$ (curve a), to 0.98 (curve b), 0.985 (curve c), 0.987 (curve d) and 0.9901 (dashed, e)

Influence of adding di-functional agent A_2 to a linear PA6

The addition of bi-functional agents to a linear PA6 is often used as flow improver^[9, 10, 14]. We test this idea in Fig. 5, by keeping constant the number of AB monomers ($= 600$) and the number of chain extremities of type B ($A_1' = 1$) and by gradually increasing the number of A_2 monomers, from 0.1 to 10 (see Fig. 5a): the more A_2 monomers are added, the shorter the chains are (see Figs. 5b and 5a), even if the proportion of double linear chains increases (see Figs. 5d and 5a). This comes from the fact that at the same time the average molecular weight of a strand decreases (see Eq. (3)) since the unbalance between ‘A’ groups and ‘B’ groups is enhanced. This larger difference between ‘A’ and ‘B’ groups leads to an important decrease of the conversion level, p_A , even if the number of chain ends “closed” by an amino group ($= N_{A_1}$) is kept constant. The plasticizing effect is thus well observed. Furthermore, it is seen that a small amount of A_2 monomers is enough in order to create a large proportion of double linear chains (see Fig. 5d: 75 wt% of double linear chains are already present if 1 A_2 is added in the specific recipe proposed here). The creation of double linear chains leads also to a decrease in polydispersity (see Fig. 5c), from 2 to 1.5^[15, 16].

Role of the A_2 agents in linear PA6 having the same number-average molecular weight

As mentioned above, adding A_2 monomers also has an impact on the sample polydispersity, which will affect the rheological behavior of the sample. Since often, the conversion level reached by solid post-condensation is limited by the molecular weight of the chains; we look here at the influence of these bi-functional agents A_2 in linear PA6 samples having the same number-average molecular weight, M_n . This last one has been fixed to 20 kg/mol. We therefore determine the conversion level of these samples in order to keep M_n constant, for

different numbers of A_2 monomers. Results are shown in Fig. 6.

In such conditions, the decrease of $M_{n,strand}$ which is usually observed when A_2 monomers are added (see Figs. 5a and 5b) is compensated by increasing the conversion level p_A . The only effect of the A_2 monomers is then to transform the linear chains into double linear chains and thus, to reduce the polydispersity from 2 to 1.5^[3, 8, 15]. As shown in Fig. 6(e), since M_n is kept constant, the zero-shear viscosity of the sample also decreases. Indeed, it is mainly influenced by the weight average molecular weight of the sample, M_w , which varies from $2 M_n$ to $1.5 M_n$. As illustrated in Fig. 7 for two different amounts of A_2 monomers ($N_{A_2} = 0.5$ or $N_{A_2} = 3$) for $N_{AB} = 600$, this has a non negligible effect on the rheological behavior of the samples.

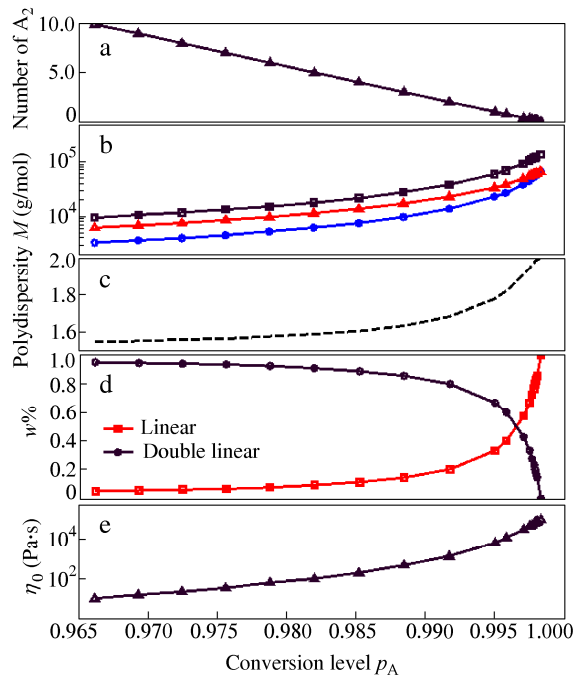


Fig. 5 Viscosity and composition of a sample containing 600 AB, 1 A_1' , and different numbers of bi-functional agents A_2 , from 1/20 to 10: (a) relation between the number of A_2 agents and the conversion level p_A , (b) average molecular weight in number ($\blacktriangle$) and in weight ($\blacksquare$) of the sample and $M_{n,strand}$ ($\bullet$) versus p_A (A_2), (c) weight proportion of linear and double linear chains versus p_A (A_2), (d) polydispersity versus p_A (A_2) and (e) zero-shear viscosity versus p_A (A_2)

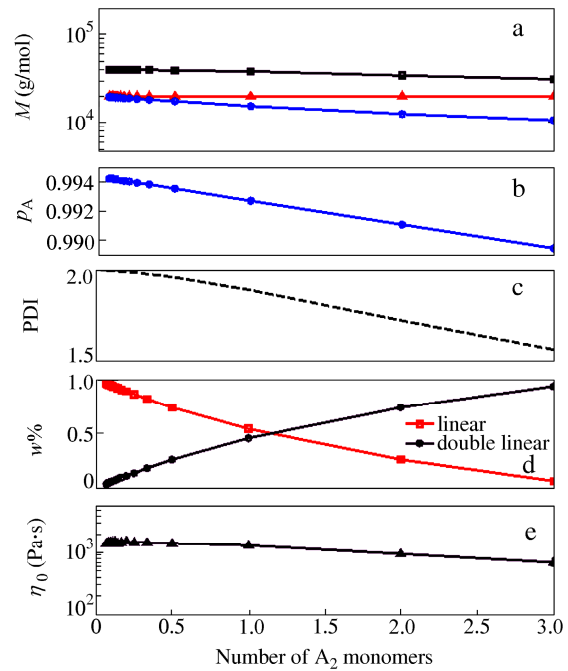


Fig. 6 Viscosity and composition of linear PA6 samples of average number molecular weight of 20 kg/mol, and containing 600 AB monomers for a number of A_2 from 1/20 to 3: (a) average molecular weight in number ($\blacktriangle$) and in weight ($\blacksquare$) of the sample and $M_{n,strand}$ ($\bullet$), (b) evolution of the conversion level used in order to keep M_n constant, (c) polydispersity, (d) weight proportion of linear and double linear chains and (e) evolution of the zero-shear viscosity η_0

Adding A_3 Tri-functional Coupling Agents to Caprolactam AB Monomers

Influence of adding tri-functional agent A_3 to a linear PA6

As observed with adding some A_2 monomers, adding tri-functional agents A_3 to a linear PA6 will induce a decrease of $M_{n,strand}$ and thus, could be seen, in principle, as plasticizer. However, as shown in Fig. 8(d), this plasticizing effect is not always observed: by adding A_3 monomers, star chains are created, which are usually characterized by relaxation times longer than the relaxation times of the corresponding double linear molecules: because of the branching point, the chains cannot reptate anymore and can only relax by contour length fluctuations^[26, 27], which are known to be slow. We therefore observe two opposite effects when a small amount of A_3 are added in caprolactam to create star-like molecules: the first effect comes from the increase of the relaxation times, which induces an increase of the zero-shear viscosity, while the second effect comes from the

fact that $M_{n, \text{strand}}$ decreases (as already observed with adding A_2), which induces a reduction of the zero-shear viscosity^[14, 26, 27]. Therefore, the sample viscosity will increase or decrease, depending on which factor is predominant.

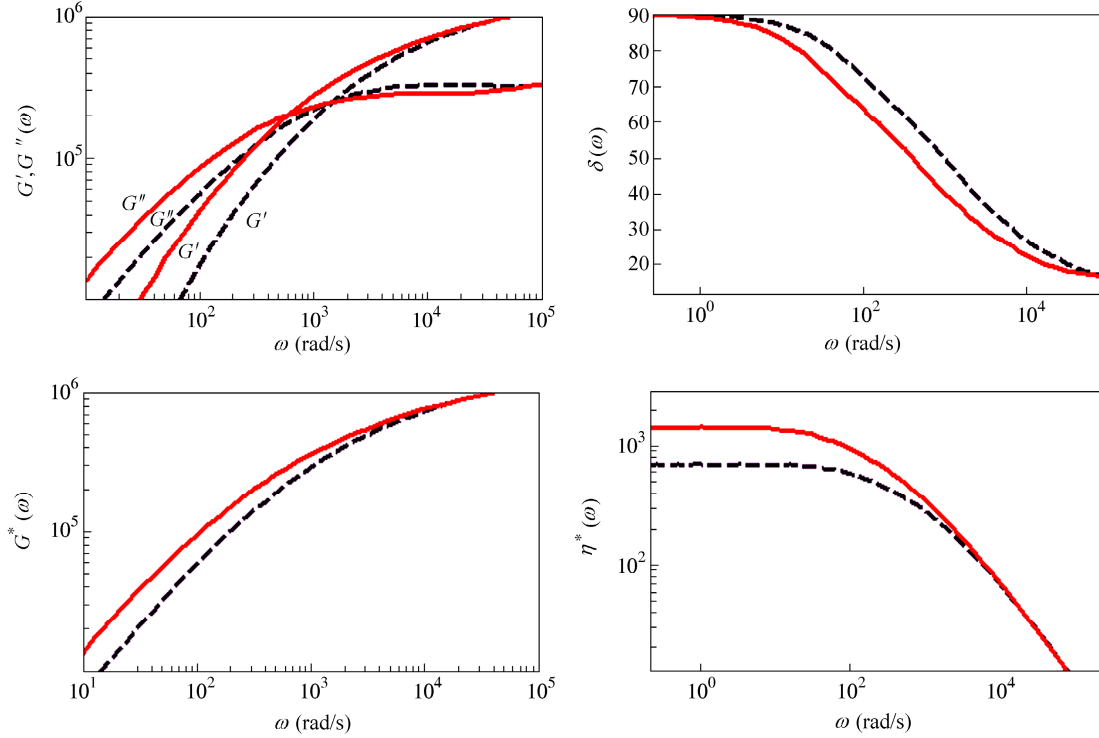


Fig. 7 Linear viscoelastic curves predicted based on the sample composition described in Fig. 6, with $N_{A_2} = 0.5$ (continuous curves) or $N_{A_2} = 3$ (dashed curves) for $N_{AB} = 600$

In Fig. 8, the results obtained by adding A_2 or by adding A_3 in PA6 are compared, keeping the same number of AB monomers ($= 600$) and of chain extremities of type B ($N_{A_1} = 1$). The number of A_2 and A_3 has been chosen in order to ensure that they have the same total number of available A groups (*i.e.* $2 N_{A_2} = 3 N_{A_3}$) and thus, the same value for $M_{n, \text{strand}}$, see Eq. (4). As observed in Fig. 8(d), the zero-shear viscosity of the system containing tri-functional agents varies in a non monotonic way in function of the number of A_3 . It is also larger than the viscosity of the corresponding sample containing bi-functional A_2 . This difference comes from the fact that the star chains cannot reptate, contrary to the double-linear chains. On the other hand, it is observed in Fig. 8(c) that the polydispersity of the samples containing A_3 monomers can be larger than two. This case corresponds to the samples which contain around 2/3 of linear chains and 1/3 of star chains (see Fig. 8c). It must also be noted that at full conversion, the polydispersity decreases from 2 to 1.33 (see Fig. 8b)^[3-5].

It must be noted that the difference in viscosity observed between the two systems should disappear in extreme cases (*i.e.* at very large number of coupling agents), when the arms are not entangled anymore. Indeed, in such condition, the chains relax according to a Rouse process, which is identical for both the star and the double linear chains of same $M_{n, \text{strand}}$ ^[25].

Based on Fig. 8, it is interesting to compare and discuss the rheological behavior of the sample containing either 0.5 A_3 coupling agent (*i.e.* $3 N_{A_3} = 1.5$) or 0.007 A_3 coupling agent (*i.e.* $3 N_{A_3} = 0.02$), for a fixed number of caprolactam and B-end groups ($N_{AB} = 600$, $N_{A_1} = 1$): these systems have indeed the same zero-shear viscosity (see Fig. 8d) but a very different composition: while the first one contains 60 wt% of star chains, has an

average molecular weight of the strands $M_{n, \text{strand}}$ of 27.1 kg/mol and an average molecular weight of $M_n = 45.3$ kg/mol, the second sample contains only 2 wt% of star chains with $M_{n, \text{strand}} = 66.5$ kg/mol and $M_n = 67.4$ k. As shown in Fig. 9, these two samples have indeed the same zero-shear viscosity. However, their shear thinning behavior is very different: the sample containing 60 wt% of star chains shows a stronger shear thinning behavior. This can be explained by the fact that the star chains are relaxing by contour length fluctuations, which leads to a much broader range of relaxation times than the samples relaxing by reptation^[26, 27]. The predictions obtained without any coupling agent are also presented in Fig. 9: while having a similar value of $M_{n, \text{strand}}$ than the sample containing 0.007 A_3 monomers, its zero shear viscosity is significantly lower. This illustrates the important influence of the star chains on the terminal relaxation of the PA6 samples.

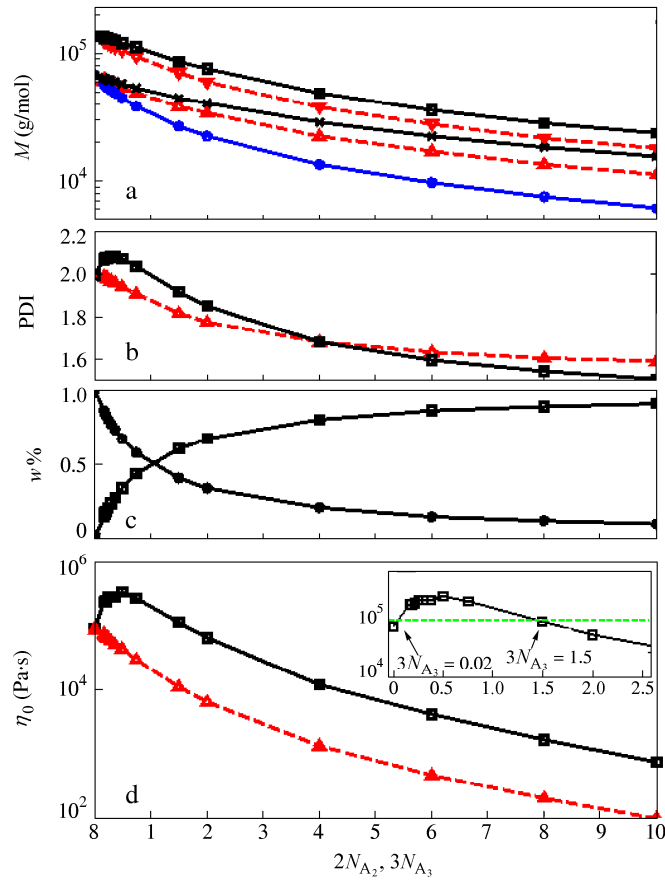


Fig. 8 Viscosity and composition of a sample containing 600 AB , 1 A_1' , and different numbers of A_2 monomers (dashed curves) or A_3 monomers (continuous curves): (a) average molecular weight in number (sample with A_3 : $\times$, with A_2 : $\blacktriangle$) and in weight (with A_3 : $\blacksquare$, with A_2 : $\blacktriangledown$) of the sample, and $M_{n, \text{strand}}$ ($\bullet$, identical for both systems), (b) polydispersity (sample with A_3 : $\blacksquare$, with A_2 : $\blacktriangle$), (c) weight proportion of linear chains ($\bullet$) and of star chains ($\blacksquare$) (For the sample containing A_2 monomers, the proportion of double linear chains coincides with the proportion of star chains) and (d) zero-shear viscosity (sample with A_3 : $\blacksquare$, with A_2 : $\blacktriangle$) and inset figure: zoom of η_0 versus $3 N_{A_3}$

Comparing these samples of same zero shear viscosity, we also observe that the average molecular weight of sample containing 0.5 A_3 coupling agents ($M_{n, \text{Strand}} = 27.1$ kg/mol, $M_n = 45$ kg/mol) is much lower than the sample mainly composed of linear chains, containing only 0.007 A_3 monomers ($M_{n, \text{Strand}} = 66.5$ kg/mol, $M_n = 67.4$ kg/mol). Since there is molecular weight limitation in the polymerization process of PA6, the use of tri-functional coupling agents can thus be a way to reduce M_n without reducing the sample viscosity. It must be

noted that conclusions drawn in the specific case presented in Figs. 8 and 9 are also found for samples with a smaller average molecular weight.

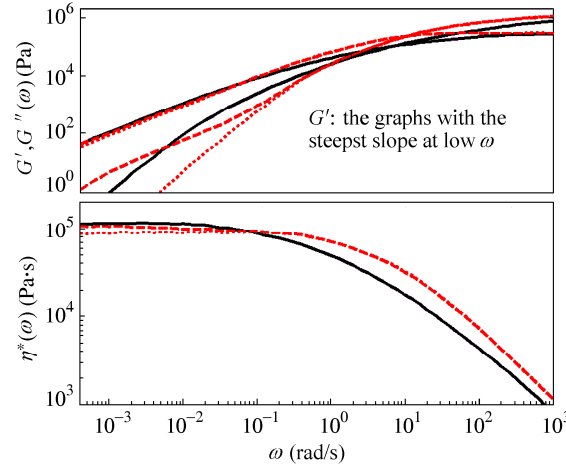


Fig. 9 Linear viscoelastic curves predicted based on the sample composition described in Fig. 8, with $3 N_{A_3} = 1.5$ (continuous curves), $3 N_{A_3} = 0.02$ (dashed curves) or $3 N_{A_3} = 0$ (dotted curves)

Influence of the Proportion of AB monomers in the recipe

As already mentioned, in order to observe a viscosity increase when adding the A_3 monomers (see Fig. 8d), the arms of the star molecules need to have a minimum length: for unentangled or poorly entangled star polymers, the suppression of the reptation process which occurs for star chains does not compensate the viscosity decrease due to the decrease of $M_{n, \text{strand}}$ ^[25–27]. Furthermore, below a certain length of the arms (around 3 entanglements per arm), star chains should relax in the same way than the corresponding double linear chains (seen as a two arm star)^[17]. Indeed, in such a case, relaxation by reptation of the double linear chains becomes negligible compared to the contour length fluctuations (for poorly entangled chains) or to Rouse relaxation (for unentangled chains): the linear chains mainly relax by contour length fluctuations, as a star chain.

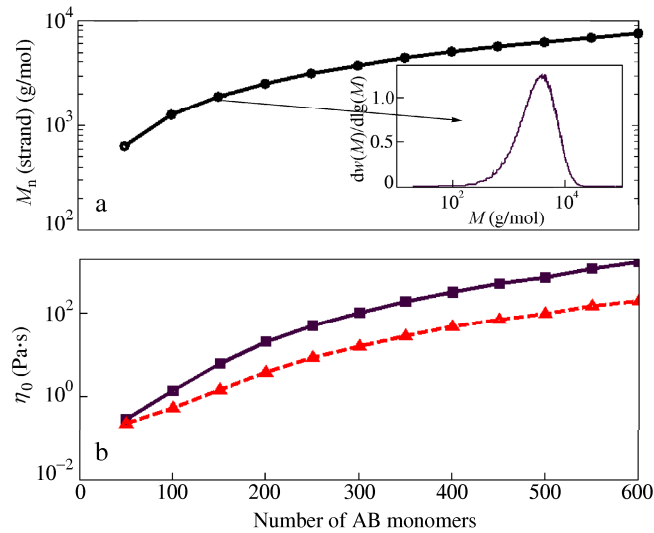


Fig. 10 Average molecular weight in number $M_{n, \text{strand}}$ (a) and zero shear viscosity (b) of a PA6 sample containing 1 A_1' and either 4 A_2 ($\blacktriangle$) or $8/3$ A_3 ($\blacksquare$), as a function of the number of AB monomers (Inset figure of (a): MWD of a strand characterized by $M_{n, \text{strand}} = 2$ kg/mol)

This is illustrated in Fig. 10 for a sample composed of 1 extremity of type B ($N_{A_1} = 1$), either 4 A_2 or $8/3 A_3$, and different amount of AB monomers. As shown in Fig. 10(a), since the number of ‘A’ groups are the same in both systems (including A_2 or A_3), the corresponding average molecular weight of a strand is identical, and depends on the number of AB monomers. As seen in Fig. 10(b), the ratio between the zero-shear viscosity of the star chains and of the double linear chains decreases by decreasing AB, to fully disappear at around $N_{AB} = 50$. This value corresponds to a rather low value of $M_{n, \text{strand}}$ (of around 650 g/mol). This is due to the sample polydispersity (of 2): the sample relaxation is very sensitive to the longer chains, which have a molecular weight much larger than this average value (see Fig. 10a)^[1].

CONCLUSIONS

A statistical approach has been developed, based on the Monte Carlo method, in order to determine the composition of a PA6 composed of AB caprolactam and some coupling agents of type A_2 or A_3 . Based on this composition, the linear rheological behavior of these samples has been predicted using the tube model developed by van Ruymbeke *et al.*^[15, 18]. This allowed us to show that while coupling agents of type A_2 can be seen as plasticizers, the effect of coupling agents of type A_3 can lead either to an increase or to a decrease of the sample viscosity, depending on the synthesis recipe and on the conversion level. By adding specific amount of these agents, we have also shown that it is possible to obtain materials with the same zero-shear viscosity but with different shear thinning behavior. Furthermore, the polydispersity of linear polymers of the same average number molecular weight, M_n , has been discussed, in function of the amount of A_2 monomers they contain. Ranging from 2 to 1.5, this difference in polydispersity is indeed expected to have a significant influence on the processing behavior of such a material.

In order to define the most suitable sample composition, these results should now be considered in view of pressure (water content) and temperature limitations of the polymerization process of PA6. Indeed, due to these limitations, a maximum conversion level can be reached, which needs to be taken into account in future simulations.

ACKNOWLEDGMENTS The authors are very grateful to K. Bronsaer and A. Nijenhuis for fruitful discussions about this work.

REFERENCES

- 1 Steeman, P. and Nijenhuis, A., *Polymer*, 2010, 51: 2700
- 2 Münstedt, H. and Laun, H.M., *Rheol. Acta*, 1979, 18: 492
- 3 Flory, P.J., *J. Am. Chem. Soc.*, 1941, 63: 3083
- 4 Flory, P.J., *J. Am. Chem. Soc.*, 1941, 63: 3091
- 5 Flory, P.J., *Chem. Rev.*, 1946, 39: 137
- 6 Hillergers, L.T., Kapnistos, M., Slot, J.J.M. and Steeman, P.A.M., *Macromol. Theory Simul.*, 2011, 20: 219
- 7 Durand, D. and Bruneau, C.M., *Macromolecules*, 1979, 12: 1216
- 8 Fradet, A. and Tessier, M., *Macromolecules*, 2006, 39: 6238
- 9 Huber, T., Pötschke, P., Pompe, G., Hässler, R., Voit, B. and Grutke, S., *Macromol. Mater. Eng.*, 2000, 280/281: 33
- 10 Scholl, M., Kadlecova, Z. and Klok, H.A., *Prog. Polym. Sci.*, 2009, 34: 24
- 11 Dai, L., Huang, N., Tang, Z. and Hungenberg, K.D., *J. Appl. Polym. Sci.*, 2001, 82: 3184
- 12 Han, H.Z.Y., Duckett, R.A., McLeish, T.C.B., Ward, N.J. and Johnson, A.F., *Macromolecules*, 1998, 31: 1348
- 13 Han, H.Z.Y., Duckett, R.A., McLeish, T.C.B., Ward, N.J. and Johnson, A.F., *Polymer*, 1997, 38: 1545
- 14 Baumann, F.E., Haeger, H., Novikova, O., Oenbrink, G., Richter, R. and Finke, M., *J. Appl. Polym. Sci.*, 2005, 96: 2413
- 15 Van Ruymbeke, E., Coppola, S., Balacca, L., Righi, S. and Vlassopoulos, D., *J. Rheol.*, 2010, 54: 507

- 16 Snijkers, F., van Ruymbeke, E., Lee, P.K.H., Nikopoulou, A., Chang, T., Hadjichristidis, N., Pathak, J. and Vlassopoulos, D., *Macromolecules*, 2011, 44: 8631
- 17 Van Ruymbeke, E., Vlassopoulos, D., Kapnistos, M., Liu, C.Y. and Bailly, C., *Macromolecules*, 2009, 43: 525
- 18 Van Ruymbeke, E., Keunings, R. and Bailly, C., *Journal of Non-newtonian Fluid Mechanics*, 2005, 128: 7
- 19 Van Ruymbeke, E., Bailly, C., Keunings, R. and Vlassopoulos, D., *Macromolecules*, 2006, 39: 6248
- 20 Van Ruymbeke, E., Muliawan, E.B., Hatzikiriakos, S.G., Watanabe, T., Hirao, A. and Vlassopoulos, D., *J. Rheol.*, 2010, 54: 643
- 21 Van Ruymbeke, E., Masubuchi, Y. and Watanabe, H., *Macromolecules*, 2012, 45: 2085
- 22 Marrucci, G., *J. Polym. Sci. Polym. Phys. Ed.*, 1985, 23: 159
- 23 Ball, R.C. and McLeish, T.C.B., *Macromolecules*, 1989, 22: 1911
- 24 Schwarzl, F.R., *Rheol. Acta*, 1971, 10: 166
- 25 Doi, M. and Edwards, S.F., “The theory of polymer dynamics”, Oxford University Press, New York, 1986
- 26 McLeish, T.C.B., *Adv. Phys.*, 2002, 51: 1379
- 27 Dealy, J.M. and Larson, R.G., “Structure and rheology of molten polymers”, Hanser Publishers, Munich, 2006