

Chain extension of polycondensates

Abstract

In this chapter the preparation high molecular weight polycondensates is described via chain extension of regular polymers during a reactive processing step, as an alternative route for the solid-state post-condensation (SSP) process. It is shown that carbonyl biscaprolactam (CBC) is a very promising chain extender.

Various polymers, such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), nylon-6 and nylon-6,6 were tested, and in all cases a strong increase of molecular weight was obtained. The viscosity level is controllable by the amount of CBC.

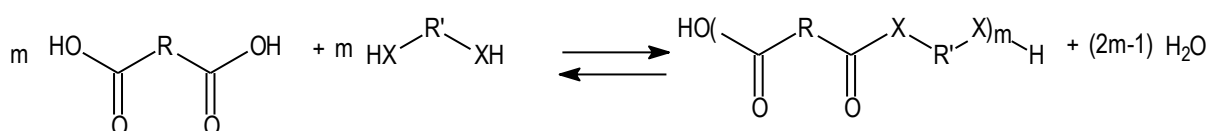
The chain extended polymers are strictly linear, according to SEC and rheology measurements. A strict linear chain extension (no chain branching) is important in many applications.

Most of the reactive extrusion work is done in the DSM micro-compounder, and some experiments are repeated in a ZSK30 extruder to confirm the results, and to improve the reliability of the translation to commercial equipments. The desired increase in molecular weight is obtained in 1 to 3 minutes, which is an acceptable time span for many applications. The resulting polymers are melt stable, since the chain extension reaction is completed within this residence time.

3.1 General introduction

3.1.1 Preparation of polycondensates

Polyesters and polyamides are prepared by a condensation reaction of diacids with diols or diamines, respectively, at temperatures between 240 and 280 °C, while removing volatiles to shift the equilibrium of the reaction in scheme 3.1 to the right.



Scheme 3.1: The preparations of polyesters (X = O) or polyamides (X = NH).

The majority of commercial polyesters and polyamides are prepared in the melt (in bulk) to avoid the costly separation of polymers and solvents and the subsequent recovery of solvents. The viscosity of the melt increases substantially during the course of the polycondensation reaction, which limits the maximally attainable molecular weight.

A second obstacle that hampers the preparation of high molecular weight polycondensates is the occurrence of side reactions that take place during the melt polycondensation step, due to the harsh reaction conditions ($T = 240\text{-}280\text{ }^\circ\text{C}$ and $\tau = 3\text{-}6\text{ h}$). Longer residence times will give more side products. Consequently, the production of high molecular weight polycondensates is difficult to realize in a melt process.

3.1.2 Solid-state post condensation (SSP)

The relative viscosities of commercial polymers such as poly(ethylene terephthalate) (PET) range from 1.55 dl/g for textile fibres to about 2.05 dl/g for industrial yarns. Low viscous grades are directly prepared in the melt, but high viscosity grades require an additional solid-state post-condensation (SSP) step. Currently, there are two types of SSP processes in use, of which one operates batch-wise and the other one continuously. Although the batch route in tumble dryers (figure 3.1) is more labour-intensive, this technology is still widely in use. In this process step the polycondensation reaction is continued by heating pellets for 20 to 50 hours in the solid state just below the melting point of the polymer, under vacuum, in a nitrogen atmosphere. The required residence time in a SSP process is rather long because of the low polymerisation temperature (about 200 °C), the low diffusion rate of the condensation water out of the pellets and because of the low mobility of end groups in the solid. This method is time and energy consuming, and therefore expensive.



Figure 3.1: Picture of a commercial solid-state post-condensation tumble dryer.

The purpose of this part of the work is to find reactive additives (chain extenders), enabling to replace the SSP process in tumble dryers by a fast chemical coupling reaction of polymer chains in an extruder, in order to make the desired viscosities in a cheaper and more convenient way.

3.1.3 Chain extension, current state

Conceptually, it would be beneficial to have a commercial route in which only a few low molecular weight grades are produced, whereas viscosities of all the other grades are tailored later on by a chemical coupling during the final processing step. To be cost competitive with the SSP process the chain extension step should be carried out in a regular extrusion step, in order to avoid additional investments. Commercial extrusion processes have residence times of 1-3 minutes (at about 300 °C), and in that short period the mixing and the chain extension reaction have to take place. The selected chemistry should consequently be very fast, not only because of the short residence times, but also because of the low concentration of end groups (about 50 mmol/l).

All considered polycondensates possess reactive end groups (OH, NH₂ or COOH), and quite a number of fast reactions are conceivable with these groups. Many chain extenders are

reported, but most of them gave side reactions (e.g. branching) due to their unavoidably high reactivity. For instance, diphenyl carbonate¹, aliphatic and aromatic bisoxazolines², bisepoxides³, diisocyanates⁴, phosphites⁵, caprolactam phosphite⁶, bisketenimines⁷, dianhydrides⁸, oxazolinones⁹ and dicyanates¹⁰ have been reported, but none of these have successfully been applied in commercial processes. Among all these potential chain extenders bislactams¹¹ are perhaps the best (no branching), and this was one of the reason to study the simplest member of this family, carbonyl biscaprolactam, in more detail.

3.2 1-[(2-oxo-1-azepanyl)carbonyl]-2-azepanone, (1,1-carbonyl biscaprolactam, CBC)

3.2.1 Bislactams

Bislactams are prepared from lactams and diacid chlorides, and in particular from caprolactam and iso- or terephthaloyl chloride (**2** and **3**, respectively, figure 3.2). Although both aromatic biscaprolactams showed promising results as chain extenders, they did not reach the commercial status so far¹¹. Nevertheless, it was our conviction that bislactams were worthwhile for further investigations. The aromatic bislactams yield a strong enhancement of the viscosity of polyesters as well as with polyamides, by reacting exclusively with OH or NH₂ groups of polymers. A further increase in viscosity is obtained if, in addition to bislactams, bisoxazolines were used, which react with the carboxylic end groups¹².

The focus of the present study is on bislactams, and particularly on the non-aromatic member of this family, carbonyl biscaprolactam (**1** in figure 3.2, CBC). This compound attracted so far only little attention in the literature, and has not been described as chain extender¹³.

The low raw material cost was an important reason to select CBC. Carbonyl biscaprolactam is prepared from caprolactam and phosgene, which is the cheapest commercially available diacid chloride.

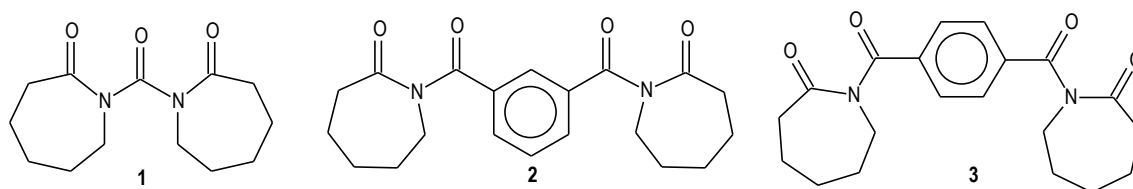


Figure 3.2: Structure of biscaprolactams of carbonic (**1**, CBC), isophthalic (**2**, IBC) and terephthalic (**3**, TBC) acid.

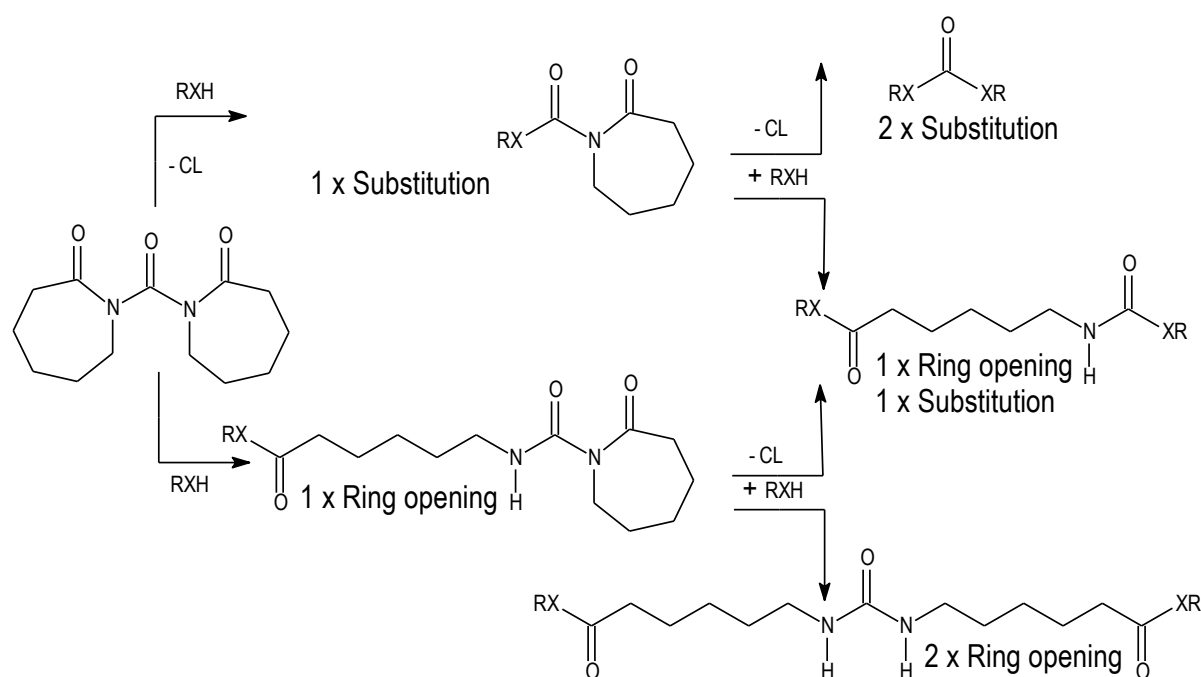
Another advantage of CBC is its low molecular weight compared to the competitive isophthaloyl and terephthaloyl biscaprolactam (IBC, resp. TBC). The molecular weight of

IBC or TBC ($M = 356$) is 41% higher than that of CBC ($M = 252$) and thus less CBC is needed when equimolar amounts of chain extender are used.

3.3 Chain extension with carbonyl biscalprolactam

3.3.1 General introduction

Chain extension of polycondensates implies that two consecutive reaction steps have to take place. First, one polymer chain end must react with the chain extender, forming a reactive polymeric intermediate. Subsequently, this reactive intermediate has to react with the end group of another polymer chain. The possible reactions that can take place between CBC and the OH or NH_2 end groups are depicted in scheme 3.2.



Scheme 3.2: The possible reactions between carbonyl biscalprolactam and hydroxy ($X = O$) or amino ($X = NH$) functional end groups of polycondensates ($\text{CL} = \epsilon\text{-caprolactam}$).

CBC can give ring opening reactions, which has not been reported for other chain extenders. In both reaction steps either a ring opening or a ring substitution can take place, leading to carbonates (2 times ring substitution), urethanes (1 time ring opening, 1 time ring substitution) or ureas (2 times ring opening).

At $T > 150\text{ }^\circ\text{C}$ –e.g. during polymer processing– the reactive polymeric intermediates will immediately react further. At lower temperatures these intermediates can be isolated, which will be discussed in the next chapters. In this chapter only the reactions at elevated temperatures are discussed, by which both consecutive reaction steps will take place¹⁴.

3.4 Chain extension of polyesters

3.4.1 Introduction

Most of the chain extension experiments were carried out in a DSM micro-compounder and some experiments were repeated in a ZSK30 extruder (paragraph 3.4.4). For this part of the study poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) were chosen, since these are the most important commercial polyesters.

Both, the mixing process (physical process) and the reaction rate (chemical process), determine the overall rate of the chain extension process. In this work the attention is mainly focussed on the chemical part. The mixing depends strongly on the type of extruder, type of screw, temperature, etc., and is, although extremely important, only briefly touched upon in this thesis.

3.4.2 Experimental conditions for chain extension of PET in the DSM micro-compounder

PET is extremely sensitive for hydrolytic degradation at high (processing) temperatures and therefore it is always dried thoroughly (48 h at 140 °C in a nitrogen atmosphere, under vacuum) before processing, and all handlings were done with great care to exclude moisture. PET pellets were ground to facilitate dosing of the polymer into the micro-compounder. CBC was added to the polymer in the glove box, either as a solid or dissolved in THF. In the latter case THF was evaporated, in a vacuum oven overnight under nitrogen at 50 °C before use. The PET samples were stored in a glove box in a dry nitrogen atmosphere before use. The samples were transported in a closed vessel and opened just before feeding the polymer to the extruder. The temperature of the extruder was raised to the set point (280 °C) and the screw speed was set at 60 rpm (revolutions per minute), before the polymer was added. It took about 45 seconds to add the polymer to the extruder and to raise the screw speed to 80 rpm. This point was taken as t_0 , the starting time of the experiment. The micro-compounder has an internal closed loop, which allows variations in residence times. The residence times were varied between 4 and 10 minutes, depending on the aim of the experiment. After a chosen residence time the micro-compounder was discharged and the strands were collected for analysis. The equipment (figure 3.3) is provided with an automatic computerized torque measurement system, which is an excellent tool to measure the reaction rate in a qualitative way. The torque data and residence times were directly collected and processed by a computer.



Figure 3.3: Picture of the DSM micro-compounder in which most of the chain extension work has been performed. On the left a view of the complete apparatus and on the right a close-up of the screws.

To verify the reproducibility five successive reactive extrusion experiments were carried out. In figure 3.4 the relative viscosity is plotted versus the residence time in the micro-compounder.

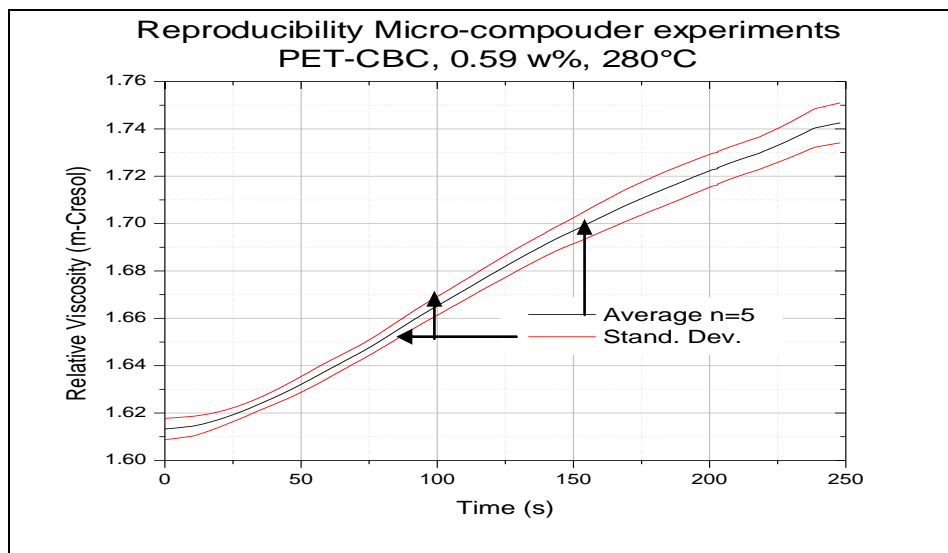


Figure 3.4: Reproducibility of chain extension experiments of PET in micro-compounder.

These relative viscosities are calculated from the empirical relation between the relative viscosity and the torque data (figure 3.5). The middle line in figure 3.4 is the average of the five experiments and the lines beneath and above this line are drawn at a distance of two σ , the standard deviation (enclosing 95.4% of the experimental data). The calculated η_{rel} was 1.74 ± 0.07 , after a residence time of 250 seconds.

The torque is a good indicator of the relative viscosity, as is illustrated by the linear relationship between the torque and the relative viscosity (figure 3.5). It was found that: $\eta_{rel} = 1.476 + (1.44 \cdot 10^{-4} \cdot \text{torque})$, in which the torque is expressed in Nm.

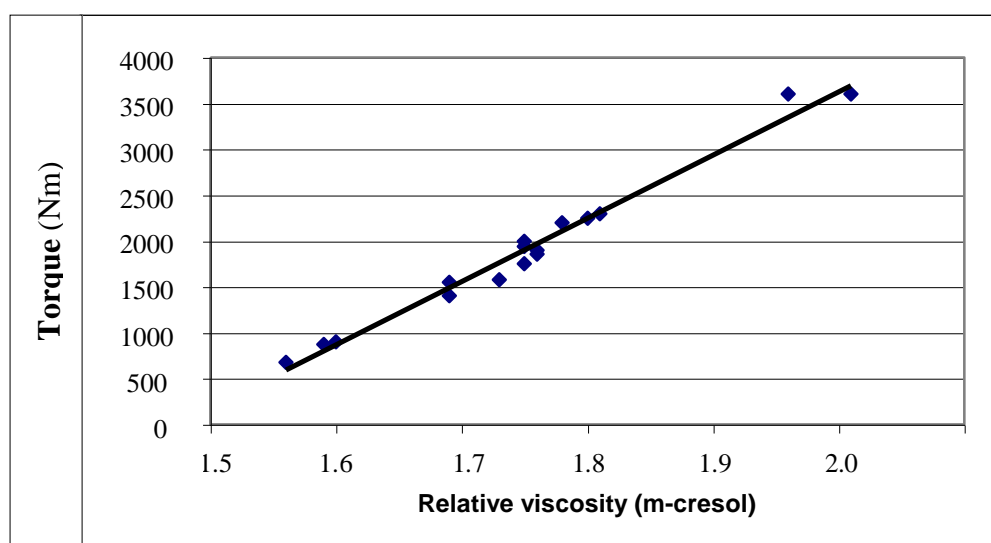


Figure 3.5: The relation between the final torque (in Nm) and the relative viscosity of PET in the micro-compounder, after processing PET with various amounts of CBC.

These results illustrate that the reproducibility of the experiments in the micro-compounder is good. When the equipment is cooled down and restarted, the absolute value of the torque may differ somewhat, but the increase of the torque, due to chain extension, is found to be reproducible.

3.4.3 Chain extension of PET with CBC

The relative viscosity of a general purpose PET grade is about 1.55 (measured in m-cresol), which corresponds with a number average molecular weight (\bar{M}_n) of about 20,000 g/mol. The concentration of carboxylic acid end groups is about 30-40 meq/kg and of hydroxy end groups is 60-70 meq/kg. CBC reacts almost exclusively with hydroxy groups, and only to a minor extent with carboxylic groups (see 2.6).

In figure 3.6 the increase of the relative viscosity is given of three commercial PET grades, with different starting viscosities ($\eta_{rel} = 1.56, 1.72$ and 1.99 dl/g), after processing with various amounts of CBC. The increase of the viscosity depends on the amount of CBC. Two base grades, with relative viscosities of 1.56 and 1.72 dl/g, would be sufficient to cover most commercial viscosities (in general between 1.55 and 2.05 dl/g) by chain extension. The maximally attainable increase in viscosity of a PET grade is limited, because CBC reacts almost only via the hydroxy groups. The rest of the end groups are carboxylic acid groups, which are hardly reactive under the conditions applied. The relation between the PET viscosity and the amount of added CBC seems to be close to linear (figure 3.6).

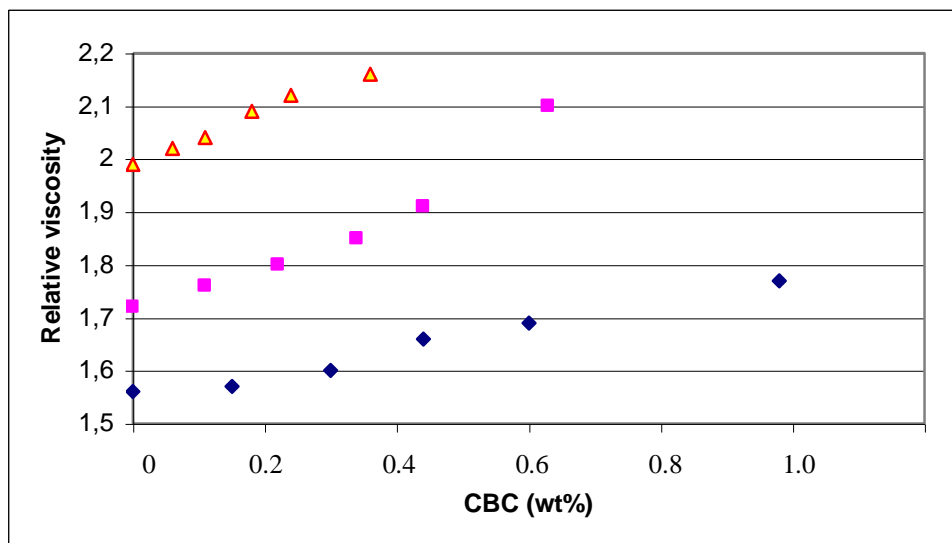


Figure 3.6: The relative viscosity of PET (in dl/g, in *m-cresol*) as function of the wt % CBC (starting relative viscosity: $\diamond = 1.56$, $\square = 1.72$, $\Delta = 1.99$ dl/g; Sample preparation: $T = 280$ °C, $\tau = 6$ min.).

However, the relation between molecular weight and solution viscosity is, according to theory, not linear. The Mark-Houwink relation ($[\eta] = KM^a$), which gives the relation between the intrinsic viscosity and the molecular weight, is an exponential relation. Thus, a non-linear relation is to be expected if the assumption is made that the molecular weight of PET increases linearly with the amount of CBC. The range of relative viscosities in figure 3.6, however, is by far too small to deviate significantly from linearity, even if a Mark-Houwink type of relation would apply.

Figure 3.7 shows a typical example of the change of the torque of the micro-compounder as function of time in a series of experiments in which PET is processed without CBC and with 0.43 (17.0 mmol/kg) or with 0.59 wt% (23.4 mmol/kg) of CBC. It can be seen that the torque of the virgin PET slightly decreases during processing, which indicates that some degradation

takes place. This is always found with PET, no matter how thoroughly the sample is dried. Similar results are obtained in commercial equipments, even under the very dry conditions as in commercial spinning units. This drop is often attributed to hydrolytic degradation, although we have not found unambiguous proof in the literature for that statement. It is more likely some thermal degradation takes place as well. Figure 3.7 demonstrates the strong increase of viscosity (torque) in time, thanks to the presence of CBC. The increase of the torque levels off after 5 to 6 minutes, indicating that the reaction is nearly completed.

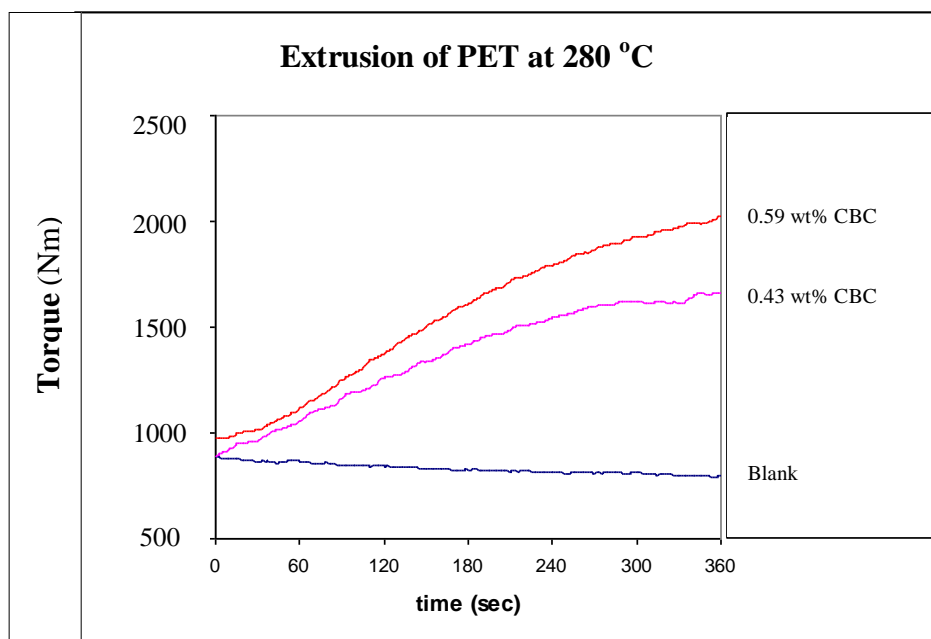


Figure 3.7: The torque during the processing of PET with CBC as function of residence time in the micro-compounder.

A residence time of six minutes is not acceptable for some applications, but the mixing capability of the micro-compounder is less than that of commercial extruders. In paragraph 3.4.4 it will be shown that the maximum viscosity of PET with CBC in a larger twin-screw extruder (ZSK30) is reached within shorter residence times.

After more than six minutes of melt processing the torque decreases slightly, in the same way as observed with virgin PET, suggesting that the newly formed linkage has a similar stability than that of the polyester backbone. This is not always the case with other chain extenders, as in literature many examples are shown, in which the stability of the newly formed linkage is insufficient¹⁵, and that viscosity drops or increases after prolonged heating or repeated extrusions.

With 0.59 wt% of CBC a higher viscosity is obtained than with 0.43 wt%, as expected (figure 3.7). 0.59 wt% (23.4 mmol) CBC is the stoichiometric amount with respect to the number of

hydroxy end groups (47 mmol/kg; notice that one mmol CBC reacts with two mmol hydroxy groups). Theoretically, the stoichiometric amount of CBC should give maximally attainable viscosity. However, as is shown in figure 3.6, the viscosity keeps increasing, even beyond the point of stoichiometry. This conflicts with theory, but it shows that under the experimental conditions the obtained level of the viscosity is an overall result, which is a combination of a viscosity build-up thanks to chain extension and a decrease due to degradation of PET. Furthermore, under these conditions CBC probably degrades to some extent as well.

More quantitative information on the chain extension of PET is given in table 3.1. It can be seen that the viscosity of the virgin PET drops during processing from 1.55 to 1.46. The concentration of the acid and the hydroxy end groups increases during processing of the virgin PET, but not in equal amounts (in mmols), indicating that the viscosity drop is not only due to hydrolysis, but also due to the well-known pyrolysis reaction. In the presence of CBC there is clearly an increase in the viscosity. To get a realistic impression of what the chain extension effect by CBC brings about, it is better to compare column 4 with 3 (virgin PET after processing), rather than 4 with 2 (virgin PET before processing). The final viscosity is the resultant of two processes: the chain extension and chain scission. The final viscosity level obtained by the chain extension process includes the degradation reactions as well.

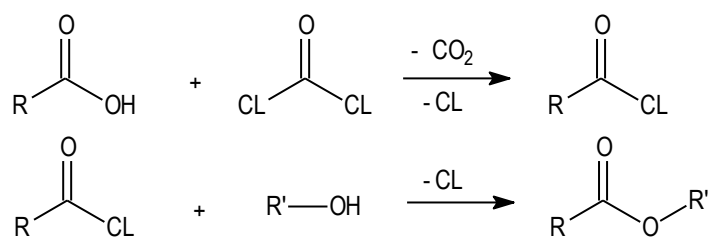
Table 3.1: End group and viscosity data of chain extended PET.

Parameter mmol/kg	Virgin PET Before extrusion	After extrusion	Extrusion with CBC (mmol/kg)
[CBC]	0	0	30
[Acid]	32	45	26
[OH]	61	68	20
η_{rel}	1.55	1.46	1.79

It can be seen that in spite of the use of stoichiometric amounts of CBC the OH concentration does not reach zero. An explanation could be that some degradation of either PET or CBC takes place or that the residence times are too short to complete the reaction.

Nevertheless, the decrease of the hydroxy groups is quite large (from 61 to 20 mmol/kg), indicating that a large part of the OH end groups have reacted. Table 3.1 shows that there is also some decrease in the concentration of acid groups. In model experiments (2.6) it was found that CBC does react with carboxylic acid groups (scheme 3.3), but at a lower rate than with hydroxy groups. In that case probably N-acyl lactams are initially formed. N-acyl lactams are activated acids that react easily with hydroxy groups, forming esters (scheme 3.3).

This reaction can contribute as well to the increase of the viscosity, but only to a limited extent.



Scheme 3.3: The formation of N-acyl lactams from CBC and carboxylic acids, followed by the conversion of N-acyl lactams into esters by the reaction with hydroxy functional compounds (CL = ϵ -caprolactam).

3.4.4 Chain extension of PET in ZSK30

To gain more information on the chain extension rate in commercial equipments some experiments were done in a ZSK30 extruder. The ZSK30 is a twin-screw extruder, which is, with respect to mixing efficiency, more comparable to commercial extruders than the micro-compounder. Dry PET pellets were mixed with 0.70 wt% of CBC, in the presence of sticking oil, and fed to the hopper of the extruder. Care was taken to exclude moisture as much as possible during these handlings. The residence time was varied by changing the screw speed (figure 3.8).

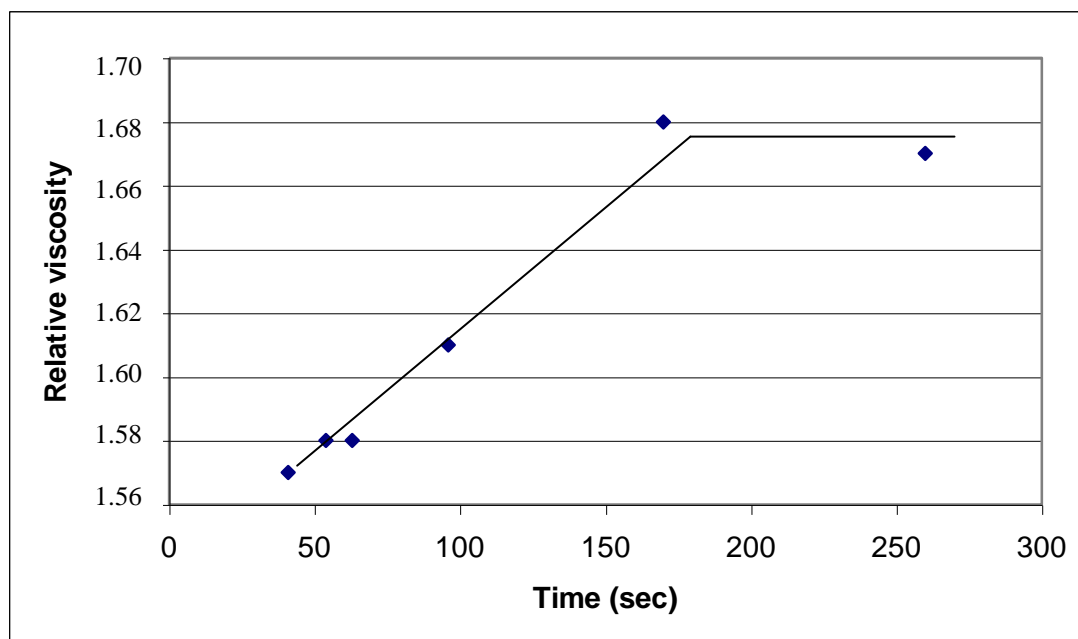


Figure 3.8: The relative viscosity (in dl/g, in m-cresol) of PET as function of residence time with 0.70 wt% of CBC in the ZSK30 extruder ($T = 270^\circ\text{C}$).

It can be seen that the plateau level of the maximally achievable viscosity is now reached in about 3 minutes, showing that the mixing efficiency of the ZSK30 is much better than that of the micro-compounder. The final viscosity level in the ZSK30 is lower than that obtained in the micro-compounder. A reason might be that it is difficult to work moisture-free (< 100 ppm water) in equipment that is not designed for that purpose¹⁾, and consequently the reproducibility of these experiments was only modest. The most important information from these experiments is that the maximum viscosity level is reached within much shorter residence times than in the micro-compounder.

A residence time of 3 minutes is still too long for some applications, and therefore the influence of catalysts was studied.

3.4.5 Chain extension of PET with CBC in the presence of catalysts

3.4.5.1 In the micro-compounder

In *chapter 2* a large series of catalysts has been screened using alcohols as model compounds. The results of these model reactions are only indicative for the reaction rate between hydroxy functional polymers and CBC. Therefore, a number of the well-performing catalysts in the model experiments were now tested for the chain extension of PET in the micro-compounder. As discussed before, the starting torque of the micro-compounder is not always exactly the same. In order to eliminate these starting variations, the torque numbers were normalized, by setting the end value on 1 (figure 3.9). The assumption was made that catalysts have only influence on the rate and not on the extent of chain extension. From the non-normalized graphs and also from viscosity measurements it was known that this influence was minor indeed.

In first screening tests Ti(OR)_4 , Zr(OR)_4 , Zr(acac)_4 and Al(acac)_3 performed well (R can be various, e.g. C_3 to C_8 alkyl groups, acac = acetyl acetonate), and amongst these, Zr(acac)_4 and $\text{Ti(OCH}_2\text{CH(C}_2\text{H}_5\text{)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{)}_4$ (Ti(2-Et-HexO)_4) were the best. Next a series of experiments was carried out with 0 to 4 mol % of these two catalysts with respect to CBC. From figure 3.9 it can be seen that the reaction rate increases by adding more catalyst. An optimal concentration of the catalyst is about 2 mol % with respect to CBC, meaning about 300 ppm with respect to PET. Adding more than 2 mol% of catalyst gives only a marginal further improvement. With Ti(2-Et-HexO)_4 as catalyst the plateau value of the viscosity is obtained in about 100 seconds, which is slightly faster than with Zr(acac)_4 . Taken the

¹⁾ In the mean time dozens of companies have tested CBC in PET in single and twin screw extruders and have found similar increases of the relative viscosity as was found in this study in the micro-compounder.

moderate mixing of the micro-compounder into account it can be concluded that a residence time of less than 100 seconds seems feasible, which is acceptable for many commercial applications. Some of the catalysts that performed well in the model reactions were not successful in the extruder experiments with PET. For instance, $MgBr_2$, which proved to be one of the best catalysts in the model reactions, was not useful with PET. This behaviour is attributed to the low solubility of $MgBr_2$ in PET. This shows that model reactions are suitable to screen a large amount of catalysts, but subsequent tests with polymers in extruders are indispensable to make the right choice. Homogeneous model reactions cannot exactly predict the kinetics of the reactions with viscous polymers in the melt.

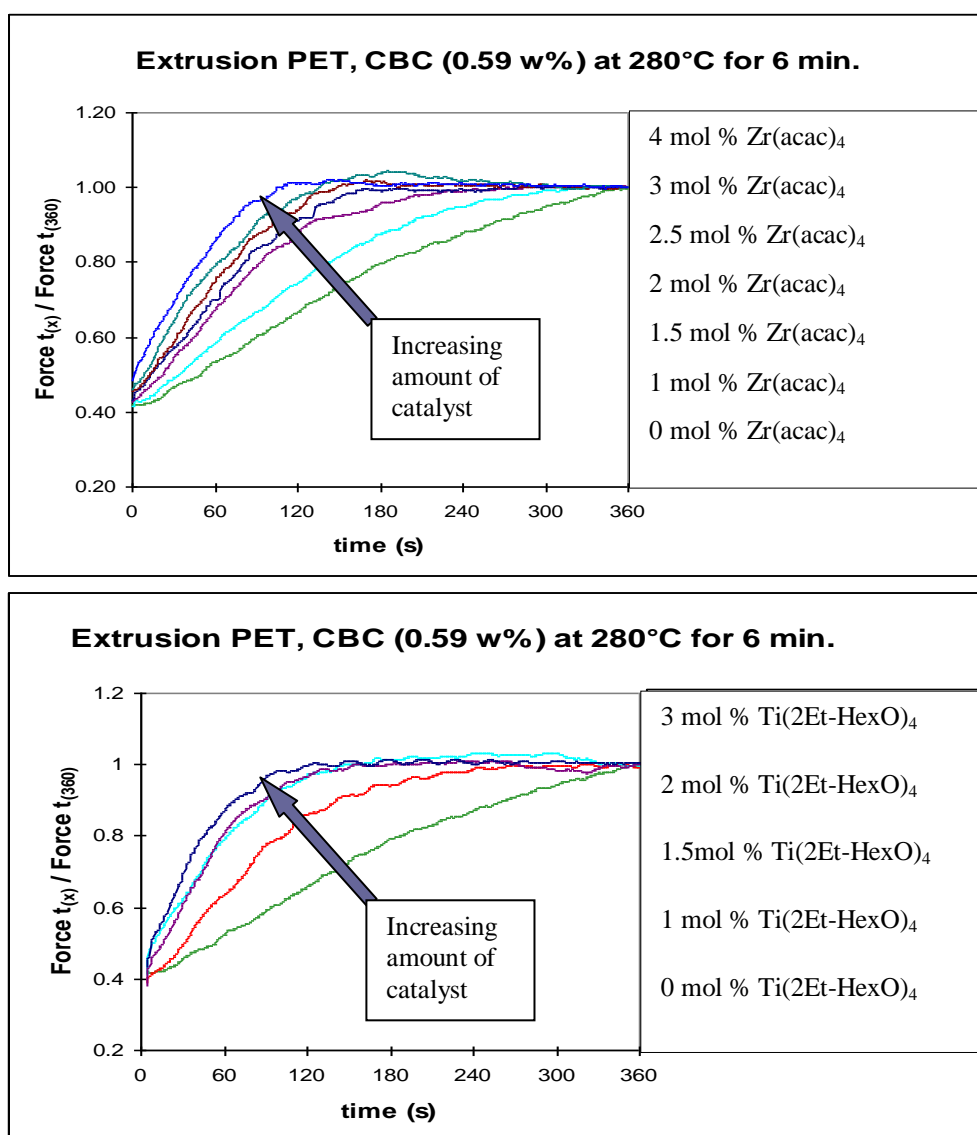


Figure 3.9: The normalized torque of the micro-compounder during the processing of PET with CBC in the presence of various concentrations of $Ti(OCH_2CH(C_2H_5)CH_2CH_2CH_2CH_3)_4$ (bottom) and of $Zr(acac)_4$ (top).

3.4.5.2 In the ZSK30

In order to get a more realistic indication of the reaction rate in commercial equipment, some experiments were done with PET in a ZSK30, in the presence of $\text{Ti}(2\text{-Et-HexO})_4$ and $\text{Zr}(\text{acac})_4$ as catalyst. A series of experiments was carried out, in which the residence times were varied by changing the screw speed, in the presence of 270 ppm of $\text{Zr}(\text{acac})_4$ or 310 ppm of $\text{Ti}(2\text{-Et-HexO})_4$ based on PET, which is 2.4 mol% with respect to CBC. From the results, shown in figure 3.10, it can be seen that the plateau level of the viscosity is now reached in about one minute, which is substantially faster than without catalyst (figure 3.8). Also here the titanium catalyst performs slightly better than the zirconium catalyst.

It can be concluded that the reaction rate in the presence of small amounts of catalyst is sufficient to be acceptable for many commercial applications. It is remarkable that the complete process, i.e. the mixing of a low molecular weight chain extender and catalyst in a highly viscous polymer melt, followed by two consecutive chemical reactions, can take place within a time span of only one minute.

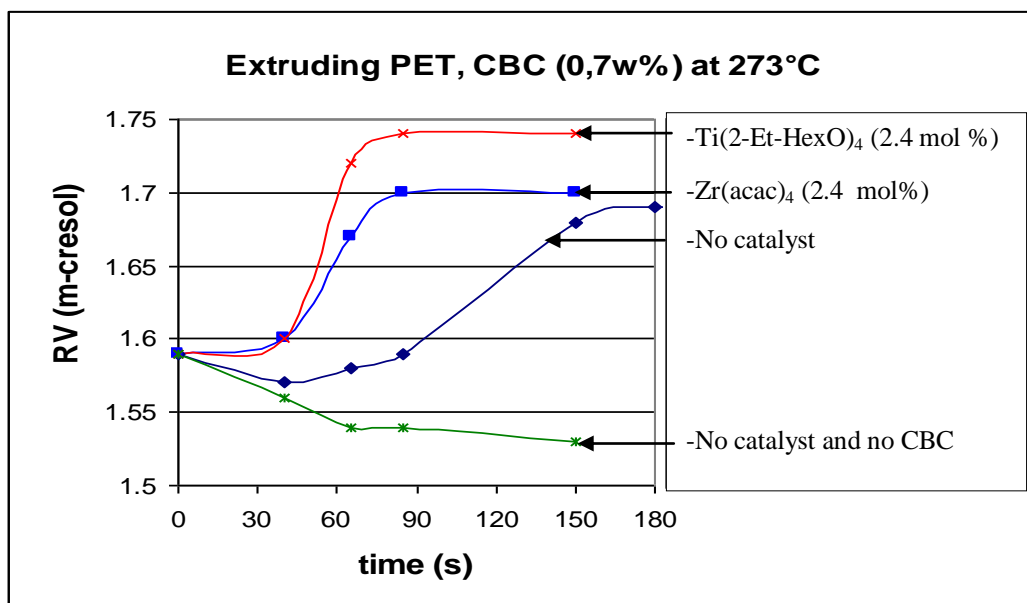


Figure 3.10: The change of the relative viscosity of PET processed with CBC in function of the residence time in the ZSK30 extruder in the presence of $\text{Zr}(\text{acac})_4$ or $\text{Ti}(\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$ (Concentration catalyst, in mol% with respect to CBC).

3.4.6 Properties of chain extended PET

One of the key issues for chain extension is that that the reactions should be fast *and* well-controlled, meaning that no chain branching should take place. In some applications branching is acceptable, sometimes even wanted, but in most applications it is not. The two

most important methods to determine the extent of branching are rheology and SEC (size exclusion chromatography), and both are used here in this work. A series of PET samples was prepared either by chain extension or by SSP, and analyzed by SEC (fig 3.11. and 3.12).

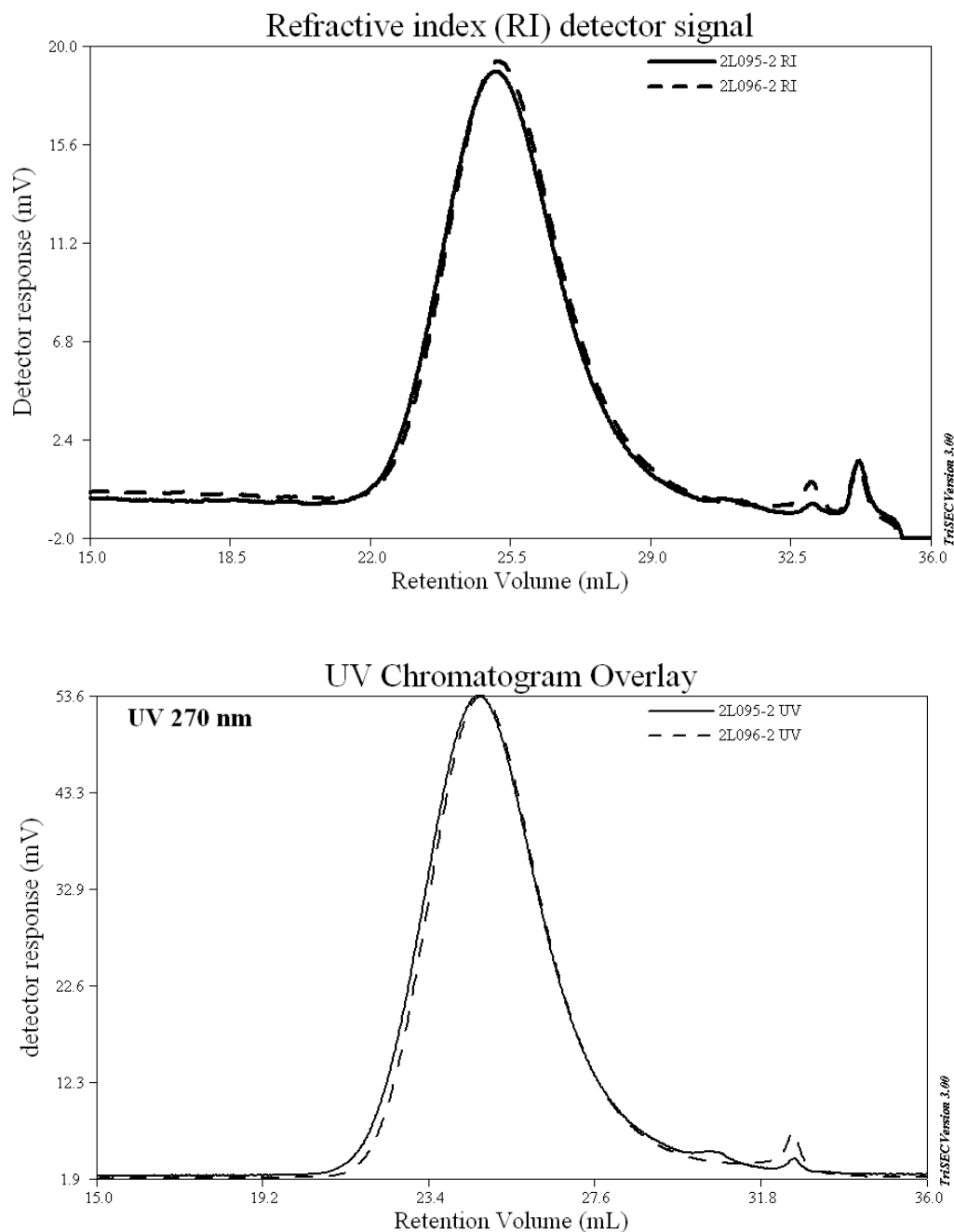


Figure 3.11: The overlays of the SEC curves of PET after chain extension (2L096, dotted line, $IV = 0.921$ dl/g, $\eta_{rel} = 1.80$ dl/g) and after solid-state post-condensation (SSP, 2L095, $IV = 0.982$ dl/g, $\eta_{rel} = 1.84$ dl/g), with UV (bottom) and with RI detection (top).

The relative viscosity of virgin PET was 1.56 dl/g, whereas the η_{rel} of chain extended PET was 1.80 dl/g and of the SSP PET sample 1.84 dl/g. The SEC measurements were carried out with RI (Refractive Index), DV (Differential Viscosity), UV (Ultra Violet light) and with LS (Light Scattering) detection.

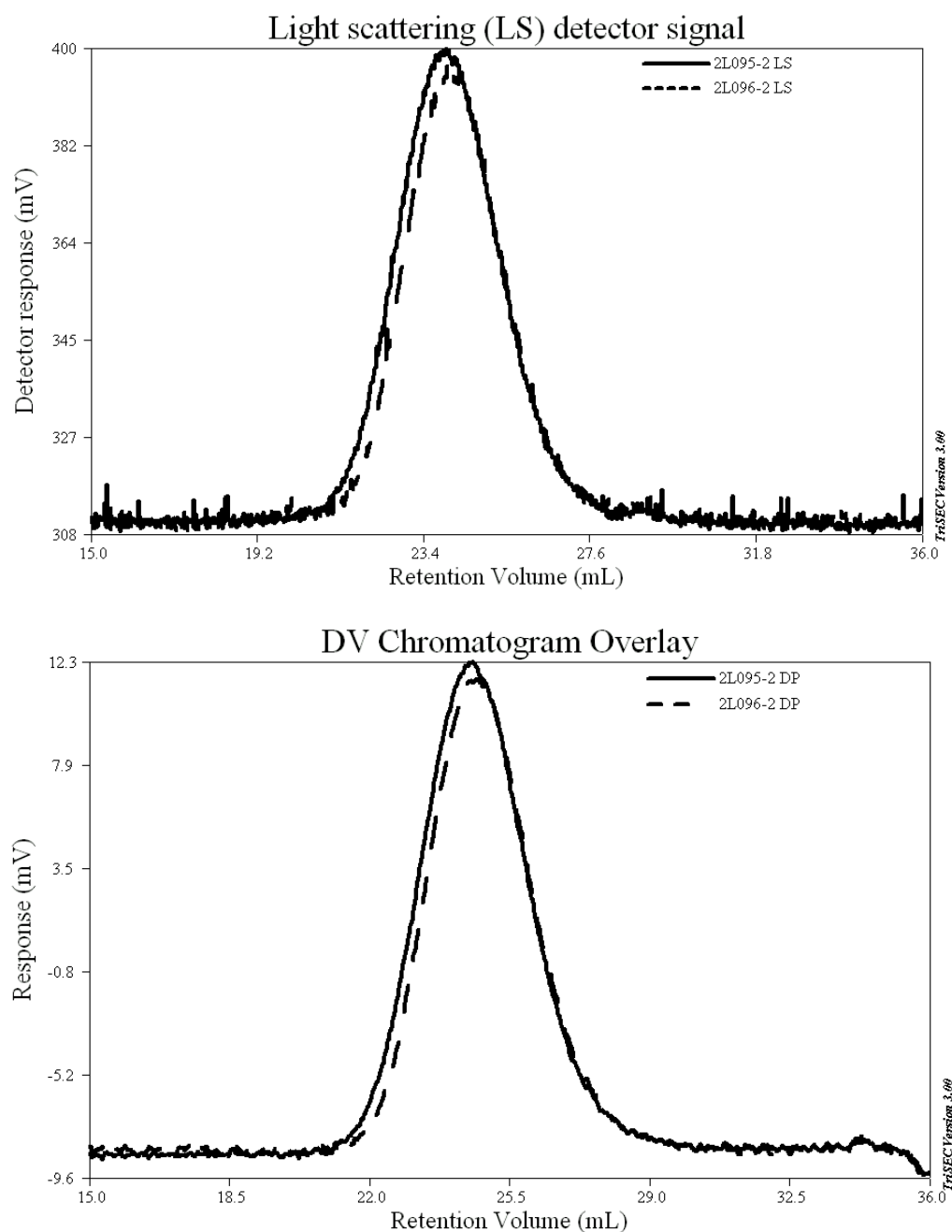


Figure 3.12: The overlays of the SEC curves of PET after chain extension (2L096, dotted line, $IV = 0.921$ dl/g, $\eta_{rel} = 1.80$ dl/g) and after solid-state condensation (2L095, $IV = 0.982$ dl/g, $\eta_{rel} = 1.84$ dl/g), with DV (bottom) and with LS detection (top).

In figure 3.11 and 3.12 curves of the molar masses and the molar mass distributions (MMD) with the various detection techniques are given and in table 3.2 the corresponding numeric values are shown. The overlays of the SEC curves show that the MMDs of SSP PET and chain extended PET are very similar, nearly indistinguishable. From the numeric values (table 3.2) it can be seen that the $\overline{M}_w/\overline{M}_n$ ratio of the chain extended PET and the SSP PET are nearly identical too (2.21 and 2.23, respectively). It is also shown in the table that the $\overline{M}_z/\overline{M}_w$ ratio and the Mark-Houwink exponent a ($[\eta] = KM^a$) are very similar and thus it can be concluded that, according to the SEC data, there is absolutely no indication of branching in the chain extended polymer.

Table 3.2: The molecular structure parameters of chain extended and SSP PET as obtained from multiple detection of SEC separations.

Sample	\overline{M}_n	\overline{M}_w	\overline{M}_z	$\overline{M}_w/\overline{M}_n$	$\overline{M}_z/\overline{M}_w$	$[\eta]$ (dl/g)	Mark-Houwink exponent a
PET 441 SSP (2L095-2)	30,000	67,000	116,000	2.23	1.72	0.982	0.69
PET BAGA + CBC (2L096-2)	28,000	62,000	101,000	2.21	1.63	0.921	0.68

Additional evidence is coming from the rheology measurements. The top graph of figure 3.13 shows the visco-elastic behavior of chain extended PET with a relative viscosity in m-cresol of 1.85 dl/g, and it can be seen that the phase angle δ goes nearly to 90° , while the slope of the relation between viscosity and frequency (shear rate) only shows a slight shear thinning behaviour, both supporting the conclusion that no detectable chain branching is observable. The visco-elastic properties of a PET sample made by SSP (with a relative viscosity of 1.82 dl/g) are given for comparison (figure 3.13 bottom), and the shape of the curves is quite similar.

More information with respect to the linearity of the chain extended polymers can be extracted from the rheology data and this is discussed in appendix B (see end of this thesis). In short, the ratio between G' (storage modulus) and G'' (loss modulus) is very sensitive for branching and for changes in the molecular mass distribution¹⁶. The data also clearly show that the chain extension with CBC does not give branching.

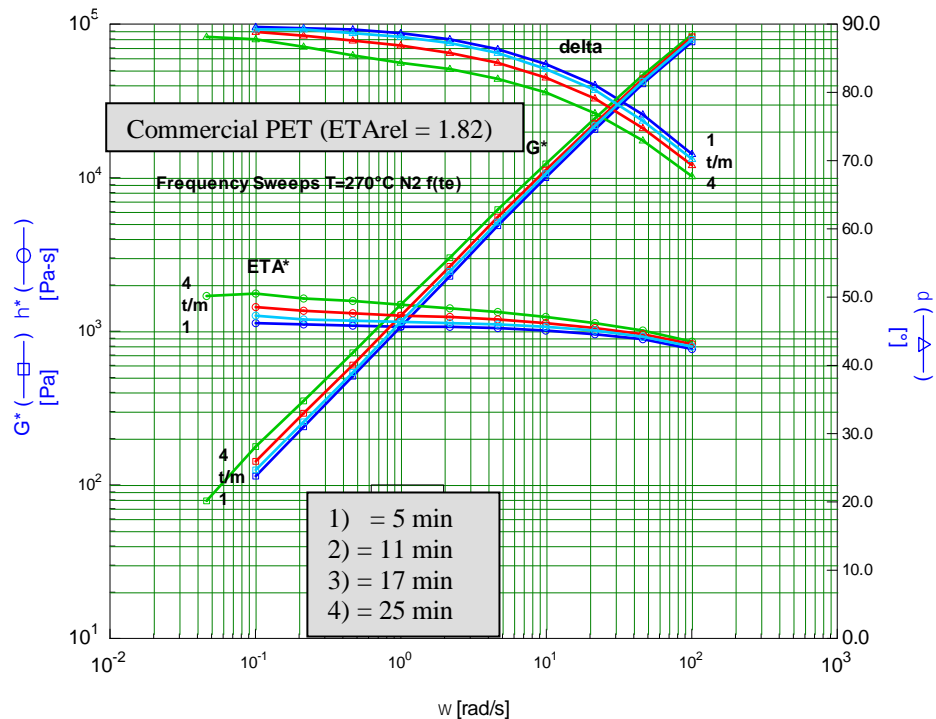
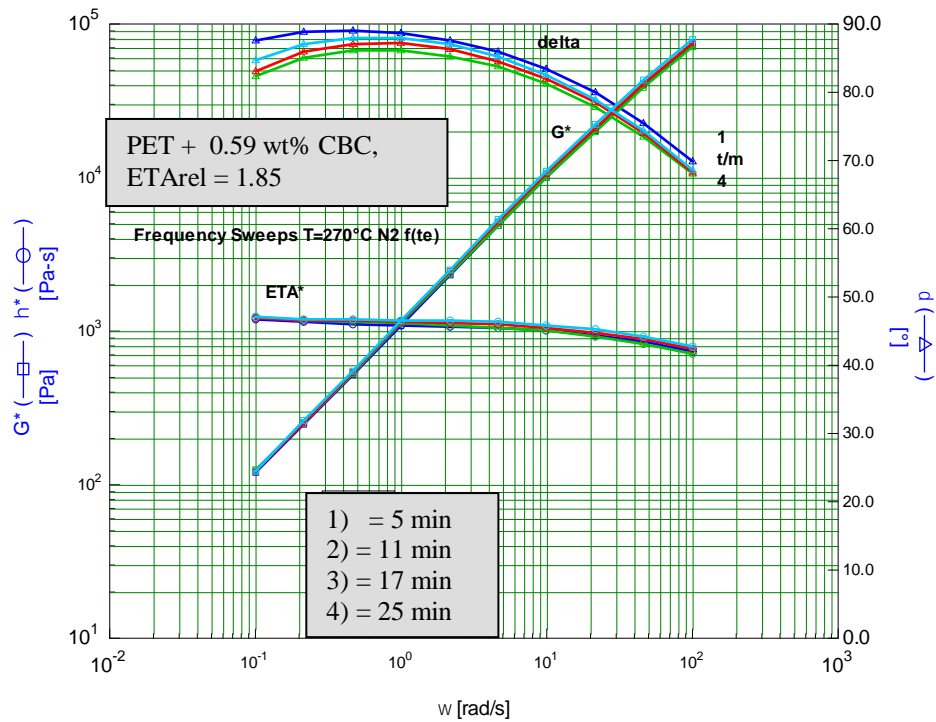


Figure 3.13: The rheology measurements (at 270 °C) of PET prepared by chain extension (top) and with SSP (bottom). In both graphs four viscosity measurements are shown, carried out after 5, 11, 17 and 25 minutes in the melt (The chain extended sample was prepared in 4 min at 280 °C).

During the measurements the viscosity of PET always gradually increases in time due to some post-condensation reactions in the rheometer. The four viscosity curves (and the four δ curves) that are shown in each of the graphs in figure 3.13 were measured after 5, 11, 17 and 25 minutes, respectively. It can be seen that the viscosity of the SSP product (bottom in figure 3.13) increases continuously, whereas the product made by chain extension hardly shows any drift of the viscosity with time, indicating that this product exhibits a higher melt stability. This favorable phenomenon can probably be ascribed to the blocking of the majority of the hydroxy end groups of the polyesters, preventing further polycondensation reactions.

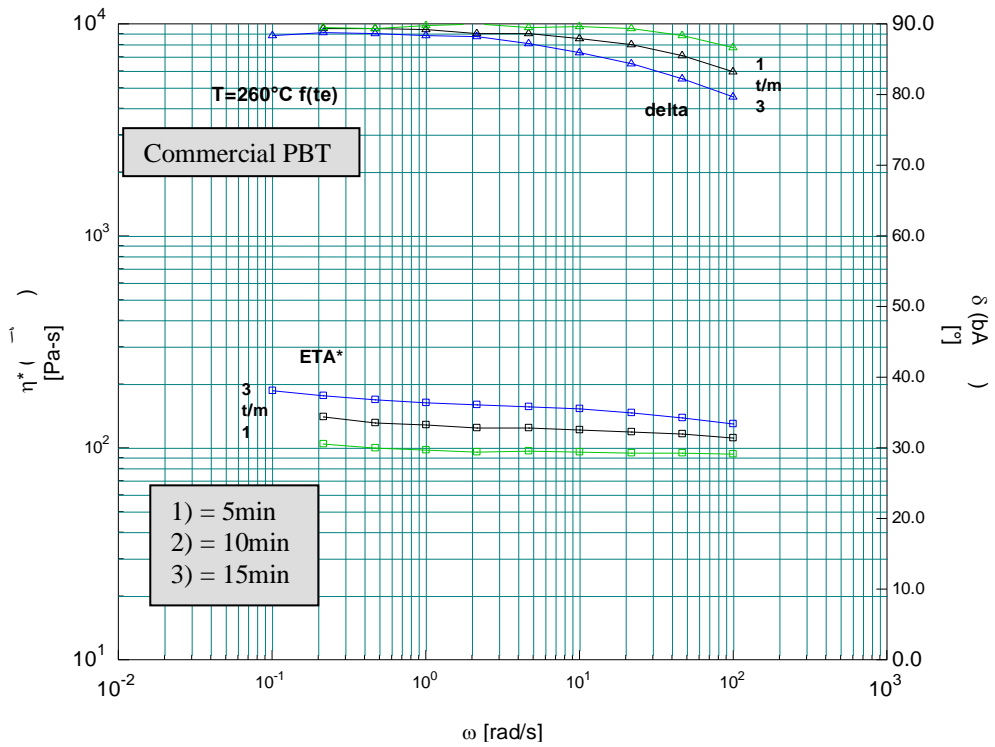
The results of both measurements, SEC and rheology, support the conclusion that there is no indication for any chain branching in the chain extended PET.

3.4.7 Chain extension of poly(butylene terephthalate) (PBT)

The feasibility to increase the viscosity of PBT by chain extension was investigated in the same way as for PET. After PBT was ground and carefully dried (24 hours, 105 °C, under nitrogen, in vacuum), CBC was added in a glove box. The concentration of hydroxy groups in PBT is higher (88 mmol/kg) than in PET with the same molecular weight, and consequently the concentration of carboxylic acid groups is lower (8 mmol/kg). The higher concentration of hydroxy groups is favourable for chain extension, since CBC reacts mainly with these groups. The experiments were carried out in the micro-compounder ($\tau = 4$ min) at 260 °C. Also in this case rheology measurements were performed to show the increase of melt viscosity and to confirm the absence of branching. In the top graph figure 3.14 the rheology of the starting virgin PBT is depicted, while at the bottom that of the chain extended PBT is given, showing two different levels of viscosities. It can be seen that the melt viscosity increases substantially from about 150 (top curve) to 400 Pa.s (bottom curve) by adding CBC (0.78 wt %, 31 mmol/kg). The phase angles δ approach nicely in both cases 90° with decreasing frequency (shear rate), indicating that no detectable chain branching has taken place. The slope of the viscosity curve of the chain extended polymers as function of the frequency (shear rate) is flat and not steeper than that of the virgin polymer, again proving that no branching takes place. The linearity of the PBT is unambiguous.

The curves 1, 2 and 3 were measured after 5, 10 and 15 min, respectively. It can be seen that the viscosity of the virgin PBT increases during these measurements, as expected. The chain extended polymer is very stable in the melt and does not increase in viscosity during the measurement. In a commercial production environment it is very important to have melt stable polymers, which consequently give a stable processing behaviour.

PBT T04201 Blank, without CBC



PBT T04201 with CBC

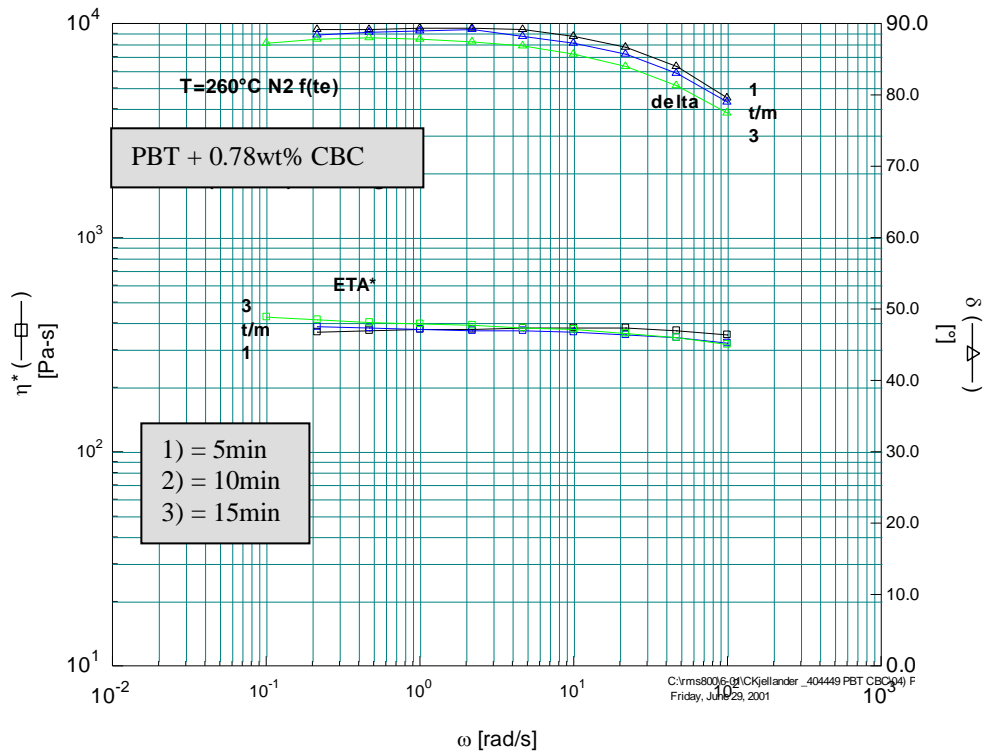


Figure 3.14: Rheology of PBT (at 260 °C) before (top) and after (bottom) chain extension (The chain extended sample was prepared in 4 min at 260°C).

One series of experiments has been done to study the influence of glass fibres on the chain extension process. PBT, with relative viscosity of 1.83 dl/g, was processed with 35 wt% of glass fibres and 1.56 wt% of CBC. After a residence time of 46 sec the relative viscosity increased to 2.34 dl/g, whereas the relative viscosity of the same composition without CBC went down to 1.78 dl/g¹⁷. These experiments clearly show that chain extension is also applicable in the presence of glass fibres.

3.5 Chain extension with two complementary chain extenders

The focus of this work is to use CBC to react with the hydroxy or amino end groups of polycondensates, whereas the carboxylic acid groups were hardly (2.6) used. But if they would be utilized too, a much more pronounced molecular weight build-up is to be expected. An indispensable condition that has to be fulfilled, to apply successfully two chain extenders simultaneously, is that they do not react with each other. Since one reacts with carboxylic acids and the other one with hydroxy or amino groups, which are complementary groups, it is conceivable, even probable, that some couples of chain extenders will react with each other.

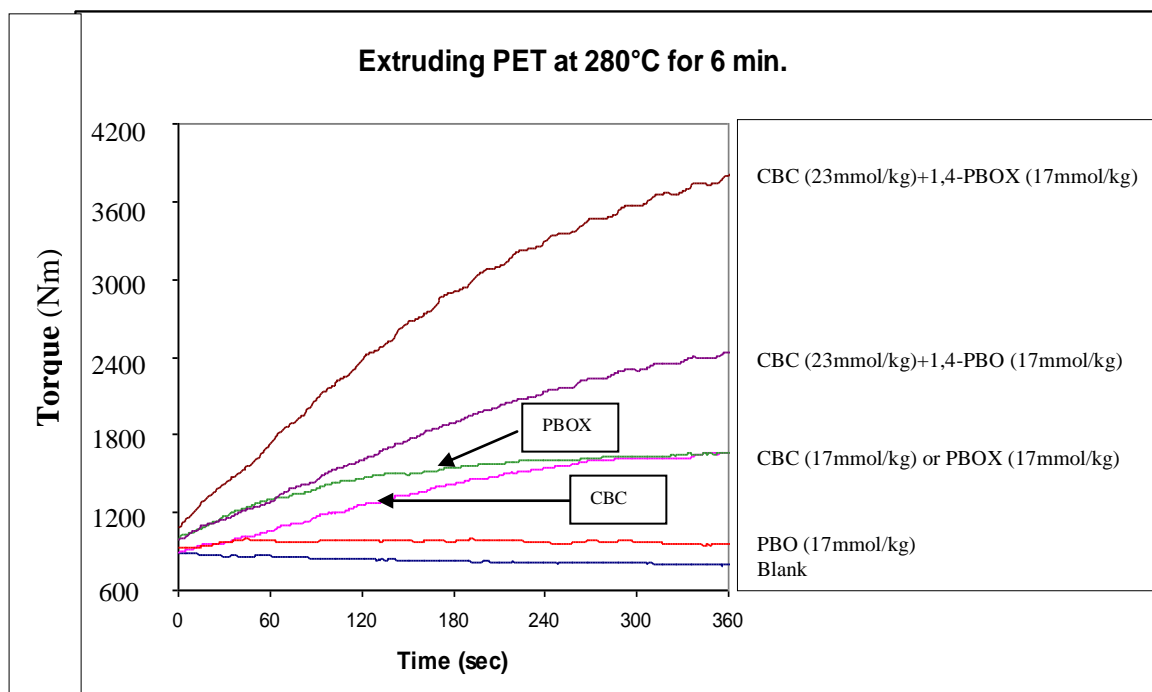


Figure 3.15: The torque of the micro-compounder during the processing of PET in the presence of CBC, 1,4-PBO, 1,4-PBOX, CBC + 1,4-PBO or CBC + 1,4-PBOX.

It was found that Phenylene BisOxazoline (PBO, **1**, fig 3.16) and Phenylene BisOXazine (PBOX, **2**) give the expected additional effect on the increase of the viscosity (figure 3.15).

The efficiency of PBOX¹⁸ is considerably better than that of PBO, which is in contrast with the results of Inata et al.¹⁹. The results are promising, but this topic is outside the scope of this work. The structures of 1,4-phenylene bisoxazoline (PBO) and 1,4-phenylene bisoxazine (PBOX) are given in figure 3.16.

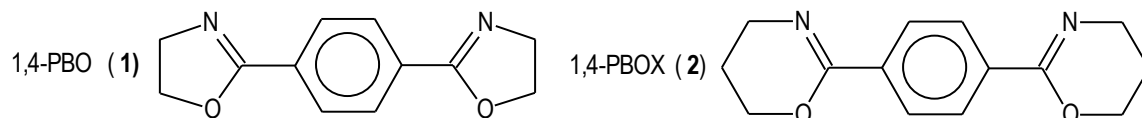


Figure 3.16: The structure of 1,4-bisphenylene bisoxazoline **1** (PBO) and 1,4-bis phenylene bisoxazine **2** (PBOX).

3.6 Chain extension of polyamides

3.6.1 Introduction

Polyamides are another important group of polycondensates that are made via a similar production processes as polyesters. Low molecular weight polymers are produced directly in an autoclave, whereas high molecular weight polymers are made in a consecutive step in a solid-state post-condensation process. Nylon-6 and nylon-6,6 are, amongst the nylons, the most important commercial polymers. A number of grades with various viscosities are available on the market to fulfil the needs. The low molecular weight grades are most frequently used, but for high duty applications higher molecular weight polymers are needed. Thus chain extension may be also for nylons an attractive alternative for the laborious SSP process.

3.6.2 Chain extension of nylon-6 with carbonyl biscalprolactam

The enhancement of the viscosity of various polyesters by CBC proceeds via a nucleophilic attack of a hydroxy end group onto one of the carbonyl groups of CBC. Amino groups are more reactive (more nucleophilic) than hydroxy groups, so a faster chain coupling reaction is to be expected with nylons than with polyesters. It is even conceivable that amide groups could react as well with CBC, giving side reactions, possibly forming branched materials.

The experiments were carried out in the micro-compounder and to facilitate dosing the commercial nylon-6 pellets were ground. After that this powder was dried during 18 h at 120 °C, CBC was added in a glove box, either as a powder or as THF solution. In the latter case THF was removed by drying the samples overnight at 50 °C in a vacuum oven, in a nitrogen atmosphere. Nylon-6 was processed with CBC for 4 minutes at 265 °C. The relation between the relative viscosity of nylon-6 (Akulon K123) and the amount of CBC is shown in figure

3.17. It can be seen that CBC is indeed able to increase the viscosity of polyamides, in a comparable way as has been shown with polyesters. The relation between the amount of CBC and the relative viscosity is apparently linear, which enables in a controlled manner the production of materials with selected viscosities.

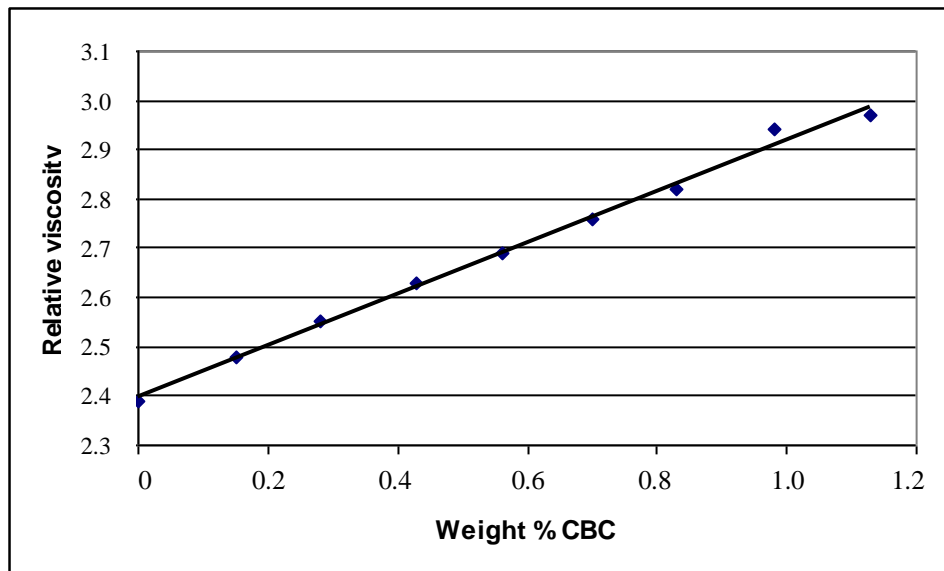


Figure 3.17: The relation between the relative viscosity (in dl/g, in formic acid/water 90/10 wt%/wt%) of nylon-6 (Akulon K123) and the amount of added CBC, after processing (Reaction conditions: $\tau = 4$ min, $T = 265$ °C).

The increase of the torque of the micro-compounder, which was an excellent tool to measure the reaction rate between polyesters and CBC, was tested here as well. It takes about 45 seconds to fill the (heated) extruder, close it and to raise the rotation speed of the screws to 80 rpm, before the measurements could be started (point t_0).

However, in this case the torque measurements (figure 3.18) show that the reaction at t_0 is already almost complete. Thus, nylon-6 reacts too fast with CBC to measure the reaction rate, yielding the desired viscosity level already in the short pre-compounding step.

Since this reaction is so fast, there was no need to study the influence of catalysts with the objective to increase the rate.

It can be concluded that chain extension is also for nylon-6 a serious alternative for the SSP process, for producing high molecular weight polymers. Starting from two base grades (e.g. η_{rel} of 2.3 dl/g and 2.8 dl/g) the whole range of commercial viscosities (η_{rel} between 2.3 dl/g and 3.6 dl/g) can be covered by chain extension.

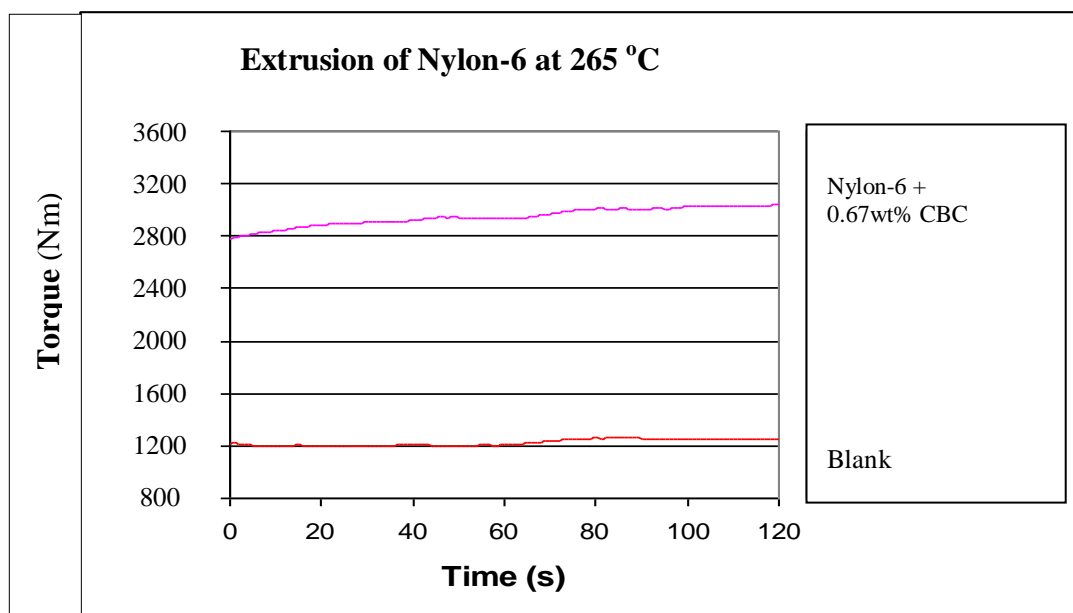


Figure 3.18: The torque of the micro-compounder during processing nylon-6 in the presence of CBC.

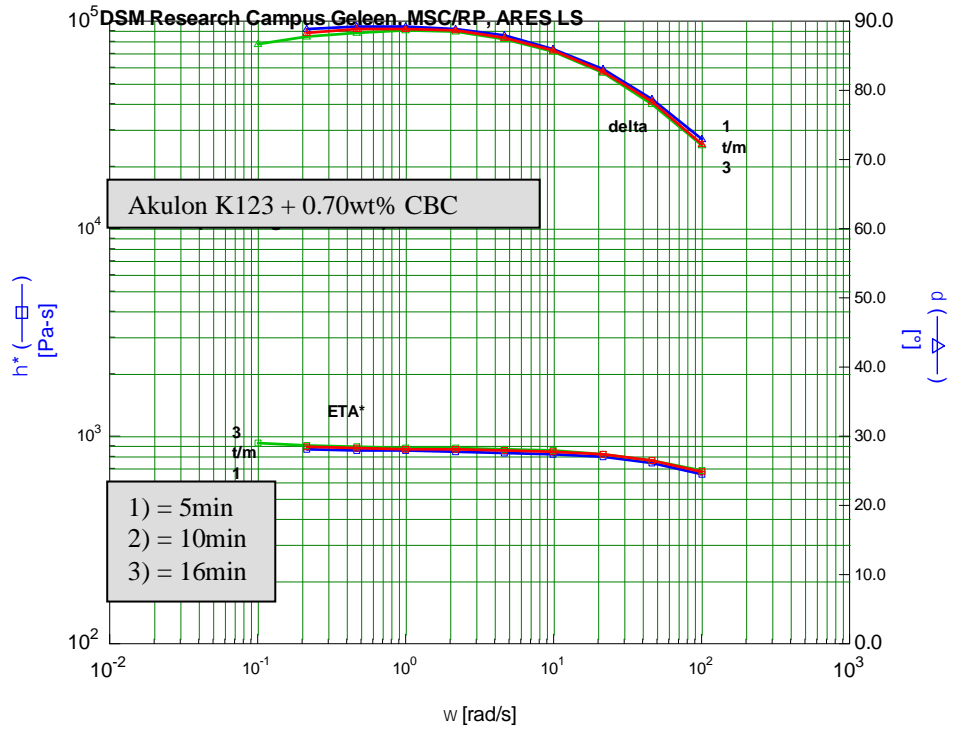
3.6.3 Properties of nylon-6

Rheology measurements were used to study the degree of branching. The bottom graph in figure 3.19 presents the data for the starting nylon-6 (Akulon K123) and the graph at the top is of the chain extended product. It can be seen that the melt viscosity substantially increases (from 400 to 900 Pa.s) by processing nylon-6 with stoichiometric amounts of CBC (0.70 wt%). The phase angle nicely reaches 90° , indicating that the chain extended product is strictly linear. The relation between the viscosity and the frequency (shear rate) has a flat slope, indicating the absence of branching as well. Apparently the amide groups have not reacted with CBC, since that would give branched polymers.

As observed for PET and PBT, the viscosity of the virgin nylon-6 polymer increases during the measurement due to post condensation reactions, whereas the viscosity of the chain extended polymer remains constant.

The most important difference between the SSP and the chain extended polymer is that the latter is actually a “copolymer”, with about 1 wt % of “comonomer”. In order to determine the influence of the “comonomer”, the thermal properties were analyzed. In table 3.3 the thermal properties of some chain extended products is given and, for comparison, also the results with some commercial products with the same range of viscosities are shown. For the preparation of these particular samples two complementary chain extenders were used. It can be seen that the first melting enthalpy of the chain extended polymer is much lower than that of the SSP product.

T = 230 °C



T = 230 °C

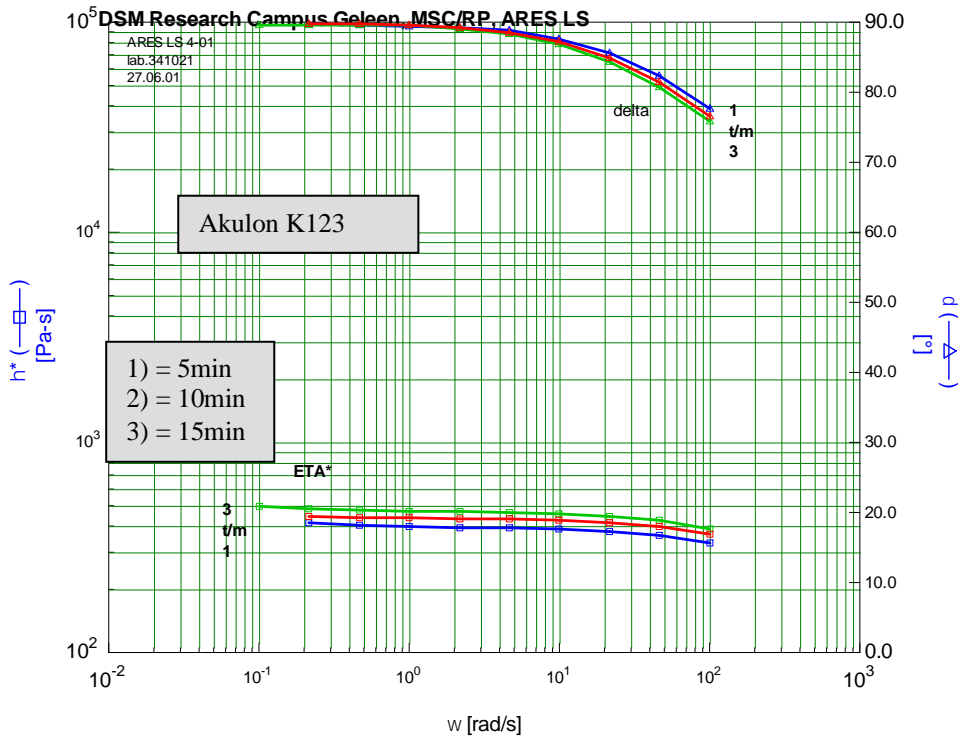


Figure 3.19: Rheology of virgin nylon-6 (bottom; Akulon K123) and a chain extended nylon-6 (top) (The chain extended sample is prepared in 4 min at 265°C).

This is to be expected, since the SSP products are heated for a long time in the solid state, which is actually an annealing procedure, giving products with a higher crystallinity. The crystallisation temperature (T_{cr}) is, in the absence of nucleating agents, strongly dependent on coincidental impurities, which makes in this case a mutual comparison unreliable. The second melting temperatures (T_{m2}) are the most important characteristics. These data show that the melting temperatures of the nylons decrease about 3 °C, after they have reacted with about 1 wt% of chain extenders. The second melting enthalpy shows that the extent of crystallisation is the same for both types of polymers, and is thus not influenced by chain extension. The decrease of the second melting enthalpy with increasing viscosity is a normal feature that is observed for virgin (post-condensated) as well as for the chain extended polymers.

The conclusion is that the “comonomers”, introduced by chain extension, have some influence on the melting temperature, but not on the melting enthalpy. The degree of crystallinity, which determines to considerable extent the mechanical properties, is therefore not affected.

Table 3.3: DSC analysis of chain extended and SSP nylon-6.

Sample	η_{rel} (dl/g)	ΔH_{m1} (J/g)	T_{cr} (°C)	T_{m2} (°C)	ΔH_{m2} (J/g)
K124*	2.52	74	189	224	70
K130*	3.00	98	176	224	64
K136*	3.60	98	176	225	61
F124 + 0.3%PBO+0.35% CBC	3.02	66	187	222	66
F124 + 0.6%PBO+0.70% CBC	3.77	66	185	221	61

*Commercial DSM grades; η_{rel} in formic/water mixture 90wt%/10wt%. ΔH_{m1} and ΔH_{m2} = Melt enthalpy of the first and second heating cycle, respectively; T_{cr} = Crystallization temperature and T_{m2} = melting temperature in second cycle; PBO = phenylene bisoxazoline.

3.6.4 Chain extension of nylon-6,6

3.6.4.1 Chain extension of nylon-6,6 with carbonyl biscaprolactam

The same experimental procedure as for nylon-6 was applied in a limited number of experiments with nylon-6,6, to show the generality of the concept for nylons. Thus, nylon-6,6 pellets were ground and dried at 90 °C for 18 h, in a nitrogen atmosphere.

CBC powder was mixed with nylon-6,6 powder in the glove box. Nylon-6,6/CBC mixtures were processed in the micro-compounder for 4 minutes at 280 °C. The increase of the

viscosity as a function of the amount of added CBC is shown in figure 3.20. The same features are observable as with the other polycondensates. A substantial increase in viscosity is obtained and the relation between the relative viscosity and the amount of CBC seems to be linear. Also in this case the relation still applies above stoichiometric amounts ($[\text{CBC}] = 2[\text{NH}_2]$) of CBC (0.55 wt%).

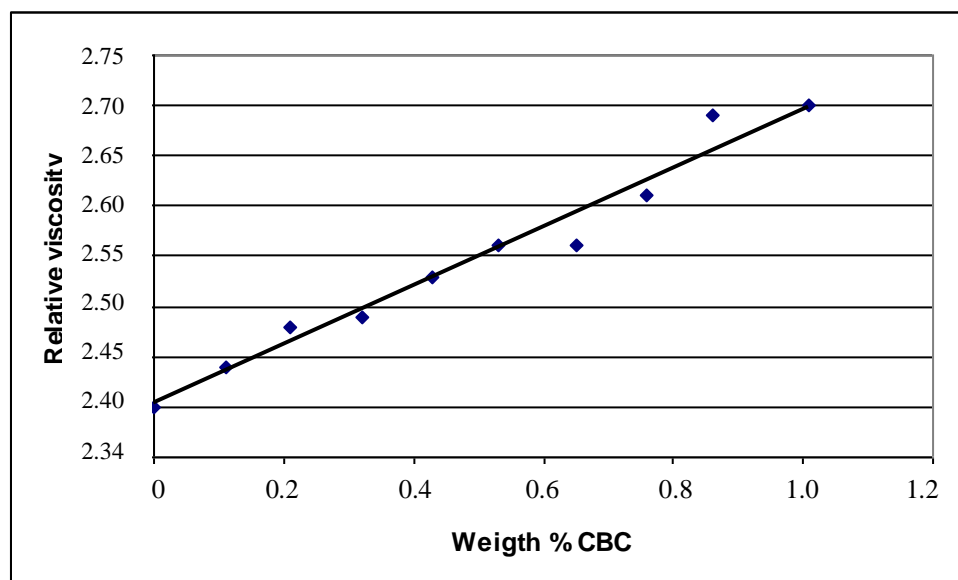


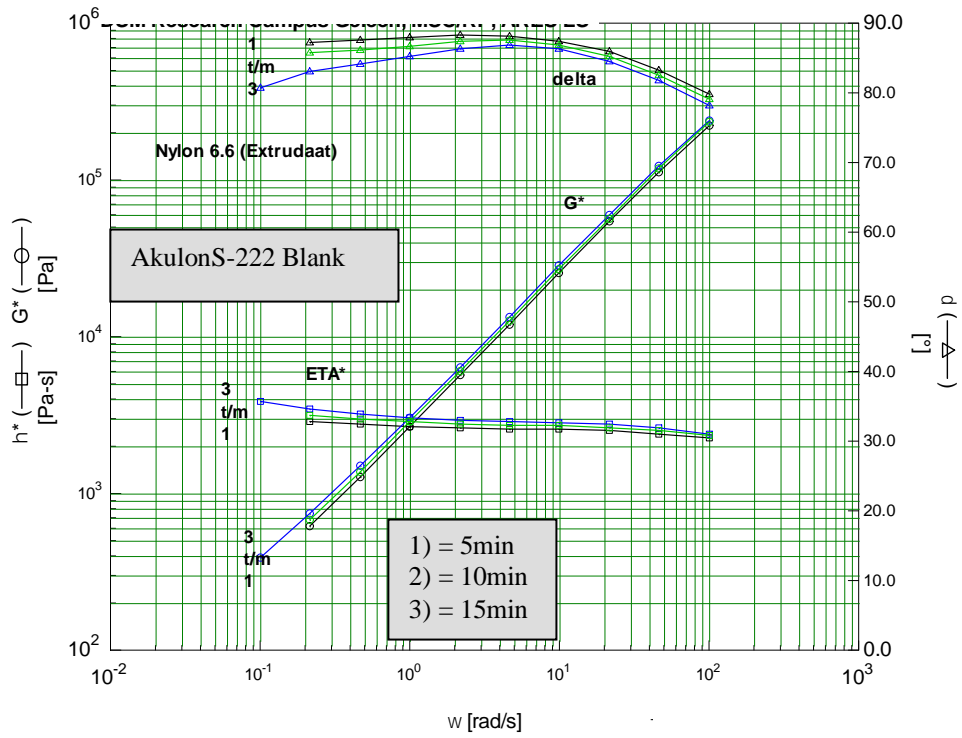
Figure 3.20: Relation between the relative viscosity of nylon-6,6 (in dl/g, in formic acid/water 90/10 wt%/wt%) and the amount of added CBC (Reaction conditions: $T = 280\text{ }^{\circ}\text{C}$, $\tau = 4\text{ min}$).

3.6.4.2 Properties of chain extended nylon-6,6

The rheology of virgin nylon-6,6 and of chain extended nylon-6,6 was measured after 5, 10 and 15 minutes of residence time in the rheometer. The phase angle for both samples is now slightly below 90° , indicating that some branching is already present in the virgin material (figure 3.21). The increase of the melt viscosity, from about 300 for the virgin nylon-6,6 to 500 Pa.s for the chain extended polymers, can be seen. The chain extended polymer has more or less the same visco-elastic behaviour as the starting sample, meaning that no additional branches have been formed. Furthermore, it can be seen that also in this case the viscosity of the chain extended polymers is more stable, although the difference is smaller than for the other polycondensates. A preliminary conclusion may be that the results for nylon-6,6 are more or less similar to those of nylon-6.

In general it can be concluded that the results with the nylons are comparable with those obtained with the polyesters. The most important difference is that the reaction rate of nylons with CBC is much higher. Thus, CBC is applicable in both types of polycondensates, in spite of the difference in end groups.

T = 270 °C



T = 270 °C

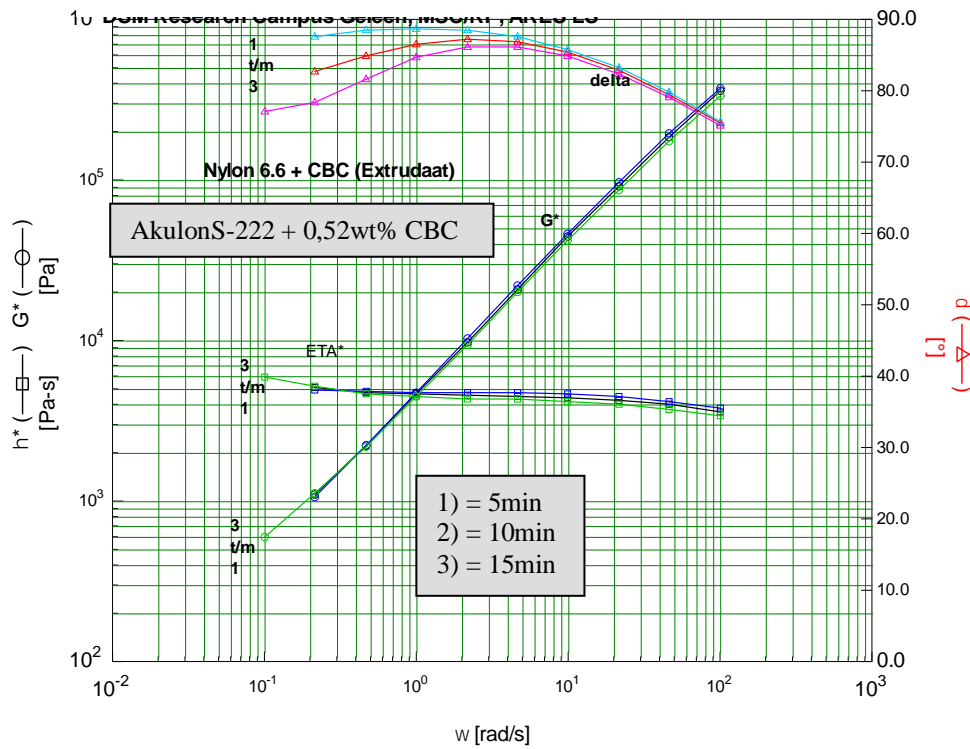


Figure 3.21: The rheology of nylon-6,6 (top) and of the chain extended nylon-6,6 (bottom). (The chain extended sample was prepared in 4 min at 280°C).

3.7 Efficiency of chain extenders

The determination of the efficiency of CBC in the chain extension reactions is difficult. The fact that the viscosity still increases if more than the stoichiometric amount of CBC is added indicates that not all the CBC is used effectively.

It turned out that a quantitative analysis of the chemistry of the polymers is difficult. Furthermore, under the harsh experimental conditions (about 300 °C) always some degradation will take place, making the reliability of the analysis even more doubtful. This is known for the polymers, but holds probably even more for reactive chain extenders. In spite of these limitations, some efforts have been done to gain insight in the efficiency of the chain extension reaction. For this purpose the concentrations of the amino and carboxylic acid end groups in nylon-6 were analyzed, before and after chain extension. These data were compared with those of a SSP product (table 3.4). The viscosities of the chain extended nylon-6 (Akulon F126) and the SSP product (Akulon F130) are not exactly the same, but close enough to allow some preliminary calculations. The concentration of CBC was matched with the concentration of the amino end groups ($[CBC] = 2[NH_2]$). In spite of this match and in spite of the fact that the reaction with nylons is expected to go to completion (figure 3.18), the concentration of the amino groups still does not go to zero. Thus even with nylon-6, which is known to be very reactive with CBC, it is not possible to consume all the amino end groups under these conditions. In contrast to PET (table 3.1), there is in this case no indication that the carboxylic acid concentration decreases. A possible explanation could be that the amino groups are much more reactive than hydroxy groups, consuming all the CBC before the less reactive carboxylic acid groups are able to react.

Table 3.4: Analytical data of the end groups and viscosities of nylon-6 (processed at $T = 265$ °C, $\tau = 4$ min).

	Blank Akulon F126	Chain extended Akulon F126	SSP product Akulon F130
[CBC] (mmol/kg)	0	29	-
[NH ₂] (mmol/kg)	58	16	38
[COOH] (mmol/kg)	52	52	45
η_{rel}^* (dl/g)	2.61	3.01	3.12

*In formic acid/water 90/10 wt%/wt%

The end group concentration of the chain extended product ($16 + 52 = 68$ mmol/kg) is significantly lower than that of the SSP product F130 ($38 + 45 = 83$ mmol/kg). This is not in

line with the viscosities, which are quite similar, although the end group modification can have some influence on the viscosity²⁰. Nevertheless, the difference in the concentration of the end groups is large and a possible explanation could be that part of the CBC has reacted only once, and is still able to react with a second chain. In that case a part of the amino groups (and CBC) is consumed, without having any effect on the viscosity. One can speculate that this difference in end group concentration of the SSP and the chain extended products ($83 - 68 = 15$ mmol/kg) is due to CBC that has reacted only once, meaning that about 50 % (15 of the 29 mmol) has not yet reacted effectively. Another rough calculation can be made as follows. The decrease in the concentration of the amino end groups ($58 - 16 = 42$ mmol/kg), due to chain extension, is twice as high as the difference of the amino end groups of F126 and F130 ($58 - 38 = 20$ mmol/kg). This suggests again that merely about half of the CBC is effective. Although both calculations are far from accurate, both indicate that the efficiency of the chain extension process is still far away from the theoretical value. Nevertheless, the practical results remain very valuable, since the viscosities of the whole range of commercial products can be covered.

3.8 Conclusion

High molecular weight poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), nylon-6 and nylon-6,6 grades have been prepared, by using chain extenders. This procedure offers a technology to circumvent the laborious solid-state post-condensation (SSP) process. A simple compound, CBC (carbonyl biscaprolactam), is found to be suitable to increase molecular weights of polymers having hydroxy or amino end groups. The reaction of CBC with polyesters is completed within 3 minutes, whereas the reaction with nylons is already finished in less than 1 minute. The amino groups of nylons are more reactive than the hydroxy groups of polyesters. The viscosity of all the polycondensates increased linearly with the amount of CBC, enabling a controlled preparation of desired viscosity levels.

The chain extension rate depends on a physical process (mixing) and a chemical process. The reaction rate in the small-scale DSM micro-compounder is about a factor two lower than in a ZSK30 twin-screw extruder. This is completely attributed to the better mixing capabilities of the ZSK30 (physical process).

To increase the reaction rate of CBC with polyesters, the influence of catalysts, selected on the basis of their performance in model reactions (*chapter 2*), was studied. It is found that tetra alkoxy titanates and zirconates and aluminium and zirconium acetyl acetonates are effective in increasing the reaction rate. Amongst these the titanium catalyst,

Ti(OCH₂CH(C₂H₅)CH₂CH₂CH₂CH₃)₄, and the zirconium catalyst, Zr(acac)₄, are particularly suitable. In the ZSK30 and in the presence of these catalysts the chain extension reaction of polyesters is completed in about one minute. The chain extension concept allows the preparation of almost the whole range of viscosities of the commercial PET, PBT, nylon-6 and nylon-6,6 grades, starting from only two base grades of each polymer.

By performing SEC and rheology measurements it is shown that all the chain extended polycondensates are strictly linear, which is important for many applications, but in particular for fibres.

In conclusion, chain extension of PET, PBT, nylon-6 and nylon-6,6 offers a valuable alternative for the currently used laborious solid-state polymerisation process (SSP).

3.9 Experimental section

Materials

CBC was obtained from DSM, New Business Development, ALLINCO[®] (purity > 99 %, HPLC) and used as received. PET grades used were: BAGA, PET441, PETA06101 from Acordis and were used as received. ARNA T04201 (PBT) and Akulon K123, F126C, F130C and F136C (nylon-6) and S222 (nylon-6,6) were obtained from DSM. All solvents and catalysts were purchased from Aldrich or Acros and used without any purification.

Instrumentation and methods

The DSM micro-compounder has a volume of 15 ml. A divisible mixing compartment containing two conical screws with a length of 150 mm forms the compounding unit. The mixing time can be varied by a re-circulation loop. The torque data were collected by an automatic data acquisition system (RS232). The set temperature was 280 °C for PET and nylon-6,6, 265 °C for nylon-6 and 260 °C for PBT. A screw speed of 80 rpm was applied. The ZSK-30 of Werner&Pfleiderer is a double screw extruder with screw diameter of 30 mm, the channel depth is 4.7 mm and the l/d value is 39. The throughput was varied from 3 to 24 kg/h, thereby changing the residence time from 180 to 40 seconds and the barrel temperature was set at 270 °C for PET (figure 3.22).

Company	Proj.Rev	Mach ID	Product	S.L.-10	B.Length	Name	Date
dsm	PET-CBC	ZSK30	pet	1324	1320	wv	03/29/2002

Description:

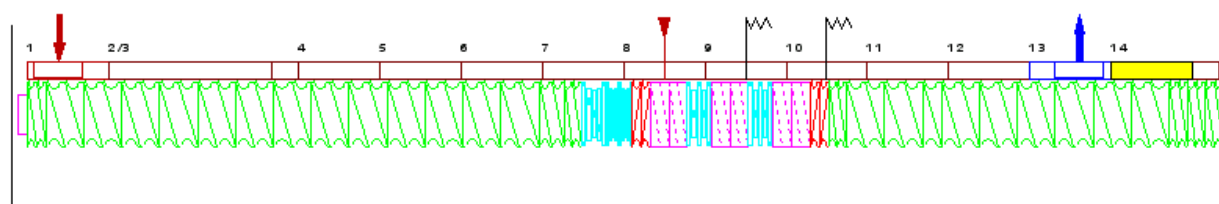


Figure 3.22: Screw design of the ZSK30.

The SEC spectra were recorded with a Hewlett Packard HP 1090 liquid chromatograph, provided with a UV-DAD detector system. The refractive index was measured with a HP 1047A differential refractometer at 35 °C and the viscosity with a Viscotek H502B at 38 °C. The Viscotek data manager was DM400. The signal of the light scattering was collected at an angle of 90 °. The column set (3 PPS PFG linear XL, 7 μ 8*300 mm) can handle the molecular weight mass ranges from 100 to 1,000,000D. The eluent was hexafluoro isopropanol (T = 35 °C) with 0.1 wt % potassium trifluoro acetate and the flow rate was 0.4 ml/min.

The computer operating system has three software systems: a) HP chemstation for the operation of the UV data of the chromatograph, b) Astra version 4.73.04 for the operation of the MALLS, c) Viscotek software TriSEC 3.0 or OmniSEC 2.0 to collect the signals and process the data.

The differential scanning calorimetry analysis was carried out on a Perkin Elmer DSC-7. Standard heating rates of 20 °C/minute were used, with samples of 5-20 mg in a dry nitrogen atmosphere.

Low frequency DMS measurements: Dynamic Mechanical Measurements were performed with a Rheometric Scientific ARES-LS dynamic analyzer equipped with ϕ 25 mm Invar parallel plate geometry. The plate-plate distance was set at 1.8 mm. Isothermal frequency scans (from 100 rad/s to 0.1 rad/s) were performed (in shear) at the appropriate temperature in a dry nitrogen atmosphere.

The DMTA measurements probe the complex dynamic modulus (G^*) and phase angle (δ) at the appropriate temperature, as function of the angular frequency (ω).

¹H-NMR was done on a Bruker ACF 300, equipped with a 5 mm dual probe head at a frequency of 300 MHz.

The relative viscosities (η_{rel}) of solutions of PET in m-cresol at concentration $c = 0.5$ g/dl were measured using an Ubbelohde viscosimeter at 25 °C. The relative viscosities (η_{rel}) of solutions of nylon-6 and nylon-6,6 in formic acid (90 wt% formic acid/10 wt% water) at concentration $c = 0.5$ g/dl were measured using an Ubbelohde viscosimeter at 25 °C.

Determination of the end groups of polyesters and nylons was performed as follows. Polyesters were dissolved in 1,1,1,3,3,3-hexafluoro-2-isopropanol (HFIP) together with 1-hexadecanol as internal standard. The hydroxy groups were esterified with antracenoil chloride and the analysis was done by HPLC with UV detection. The concentration of the amino groups in polyamides was determined by dissolving the nylons in m-cresol and by titration of the amino groups with ethanolic HCl solution. The titration was followed by means of potentiometric detection electrodes.

Carboxylic acid groups of polyesters were determined by dissolving the polyesters in o-cresol/2-t-butylphenol, after diluting the solution with chloroform the mixture was titrated potentiometrically with tetrabutyl ammonium hydroxide in 2-propanol. Carboxylic groups in polyamides are determined by dissolving the samples in 2-t-butylphenol. After diluting the solution with chloroform the mixture was titrated potentiometrically with tetrabutyl ammonium hydroxide in 2-propanol.

Synthesis

Sample preparation of PET (drying, grinding, CBC addition)

Pellets of PET were ground in a SPEX 6750 Freezer mill. Then this polymer was dried at 140 °C for 48h under vacuum (< 200 mbar) in a nitrogen atmosphere. CBC was added as a powder or dissolved in THF (1 wt% CBC in THF) and then an appropriate amount of the powder or THF solution was added to the ground PET in a glove box under a nitrogen atmosphere. The

samples prepared via the solution route were subsequently dried at 50 °C for 18 h under vacuum (< 200 mbar) in a nitrogen atmosphere, and stored in the glove box until use.

Sample preparation of PET with catalysts

For the preparation of samples with catalyst the same procedure was followed as described above. The catalyst was added to the same THF solution in which CBC was dissolved.

Sample preparation of PBT

PBT pellets were ground in a SPEX 6750 Freezer mill. Then this polymer was dried for 24 hours at 105 °C, in vacuum (< 200 mbar) in a nitrogen atmosphere. CBC powder was added in an appropriate amount to the ground PBT in a glove box under a nitrogen atmosphere. The samples were stored in the glove box until use.

Sample preparation of nylon-6

Pellets of Akulon K123, Akulon F126C, Akulon K130C and Akulon F136C were ground in a SPEX 6750 Freezer mill. Then this polymer was dried at 120 °C for 18h under vacuum (< 200 mbar) in a nitrogen atmosphere. CBC was added as a powder or dissolved in THF (1wt% of CBC in THF) and then an appropriate amount of this solution was added to the ground nylon-6 in a glove box under a nitrogen atmosphere. The samples prepared via the solution route were dried at 50 °C for 18 h under vacuum (< 200 mbar) in a nitrogen atmosphere, and stored in the glove box until use.

Sample preparation of nylon-6,6

Pellets of Akulon S-222 were ground in a SPEX 6750 Freezer mill. Then this polymer was dried at 120 °C for 18h under vacuum (< 200 mbar) in a nitrogen atmosphere. CBC was added as a powder or dissolved in THF (1wt% of CBC in THF) and then an appropriate amount of the powder or of the THF solution was added to the ground nylon-6,6 in a glove box under a nitrogen atmosphere. The samples prepared via the solution route were dried at 50 °C for 18 h under vacuum (< 200 mbar) in a nitrogen atmosphere, and stored in the glove box until use.

Handling of the micro-compounder

The DSM micro-compounder was heated to the appropriate temperature (280 °C for PET and nylon-6,6, 265 °C for nylon-6 and 260 °C for PBT). While dosing the polymer powder the screw speed was set to 60 rpm (revolutions per minute). After dosing had been completed (about 45 sec) the screw speed was increased to 80 rpm and that point was taken as the start of the experiment t_0 . During the compounding step the torque on the screws was measured continuously and the data were collected and processed by a computer. The micro-compounder was discharged after the appropriate compounding time (mostly between 4 and 6 minutes) and the strands were collected for further analysis.

Handling of the ZSK30 extruder

PET pellets were dried in a tumble dryer (12h at 140 °C in a dry nitrogen atmosphere) and packed in sealed bags to prevent the up-take of moisture. Next, the pellets were tumbled in a drum roller under dry nitrogen and CBC was stuck onto the pellets by using 0.1 wt % of Primol 352 oil. If catalysts were used, they were mixed with CBC in a glove box under dry nitrogen. The feeder and the inlet of the ZSK30 were flushed with dry nitrogen, while a plastic foil covered the hopper. The barrel temperature was set at 270 °C, and the temperature of the polymer melt was 273 °C. The screw speed was set at 100 rpm and the throughput was between 2 and 24 kg/h, resulting in different residence times. In these experiments a standard screw design was used as depicted in figure 3.22.

3.10 References

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