

End group modification of polyamide-6 in supercritical and subcritical fluids

Part 2: Amine and carboxylic acid end group modification with 1,2-epoxybutane

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Received 10 September 2002; received in revised form 17 March 2003; accepted 17 March 2003

Abstract

The amine and carboxylic acid end groups of polyamide 6 (PA-6) granules were blocked with 1,2-epoxybutane in supercritical or subcritical fluids. The fluids were mixtures of either propane or CO₂ with 10 mol% 1,4-dioxane. Temperatures of 50–140 °C and pressures of 70–80 bars were applied. The reactions were followed in time. The modified polyamide samples were analysed by carboxylic acid end group titrations, by FTIR spectroscopy, by solution and melt viscosity measurements, by DSC and SEC/DV. End group concentrations, relative viscosities and molecular weight distributions (MWD) of modified samples were compared with corresponding values of unmodified PA-6. It was found that better blocking of the end groups was obtained with increasing reaction temperature. However, after modification, at higher temperatures, a decrease in relative viscosity was found. SEC measurements showed that this decrease in relative viscosity not necessarily implies that chain scission had occurred, but that it must be the result of a different interaction of the modified polymer end groups with the solvent. Best results were obtained for PA-6 modified at 100 °C in propane/1,4-dioxane: an improved melt stability was obtained without discolouration of the PA-6 granules or a change in molecular weight, due to the blocking of the amine end groups but leaving the majority of the carboxylic acid end groups unblocked.

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Keywords: Supercritical fluids; Polyamides; Carboxylic acid end group modification; Melt stability

1. Introduction

Supercritical fluids (SCF), especially supercritical CO₂ (scCO₂), have interesting properties [1] and,

are therefore, frequently used in polymer modification processes. SCFs can act as a plasticiser for a variety of polymers [2,3]. Due to the plasticising effect of the SCF, the mobility of the amorphous polymer segments will be increased. The enhanced mobility of the polymer chains results in, for example, an enhanced extraction of low molecular weight material from the polymer, but it may also

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facilitate the impregnation of solid polymer particles with chemical reagents. From an environmental point of view, scCO_2 is a benign alternative for organic solvents. However, a disadvantage of scCO_2 is its apolarity, which makes it a poor solvent for polar solutes, and the swellability of relatively polar polymers by CO_2 , favourable for extraction, is limited. Nevertheless, Muth et al. [4] and Berens et al. [5] succeeded in polymer modification by supercritical impregnation.

Contrary to the results described in Part 1 of this series of papers on the modification of end groups of PA-6 in supercritical and subcritical fluids [6], the present work describes the blocking of both the amine and the carboxylic acid end groups. This time 1,2-epoxybutane was used as the blocking agent, which was impregnated at relatively mild conditions into the swollen polyamide granules where it was able to react with either one or with both types of end groups, depending on the applied reaction conditions. The aim of blocking the end groups of PA-6 by impregnation of the blocking agent under relatively mild reaction conditions via SCFs, is to avoid undesired side reactions, possibly occurring in the melt, such as chain extension. The end capped polyamides are expected to exhibit an enhanced melt stability during processing, implying the constant molecular weight distribution (MWD), required for stable spinning and extrusion processes.

2. Experimental

2.1. Materials

Polyamide 6 (PA-6) granules of the type Akulon F124 (film grade) were kindly supplied by DSM Research, the Netherlands. These granules had an amine end group concentration of $55 (\pm 2)$ mmol/kg, a carboxylic acid end group concentration of $53 (\pm 2)$ mmol/kg, and a relative viscosity in 90 wt.% formic acid (η_{rel}) of $2.47 (\pm 0.02)$. 1,2-Epoxybutane was purchased from Aldrich. Chloroform, *m*-cresol (97%), chloroform-*d*, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and 2,2,2-trifluoroethanol (TFE, 99.8%) were purchased from Acros Organics. 1,4-Dioxane and concentrated HCl were purchased from Merck, CO_2 (purity 4.5) was purchased from Hoekloos and

propane (purity 3.5) from Messer–Griesheim. All chemicals were used as received.

2.2. Modification of PA-6 with 1,2-epoxybutane in supercritical or subcritical media

Approximately 15 g of granules of PA-6 and 1.12 g of 1,2-epoxybutane (a 10-fold excess based on the sum of the amine and carboxylic acid end groups of PA-6) were put in a glass tube, which was placed in a 50 ml high-pressure cell (pressure maximum is 850 bars). After closing the high-pressure cell, the fluid (being either propane or CO_2 , with 10 mol% 1,4-dioxane) was added. The desired pressure and temperature were obtained by first raising the temperature and subsequently increasing the amount of fluid. The modification was performed in either sub- or supercritical mixtures of propane and 10 mol% 1,4-dioxane, or in sub- or supercritical mixtures of CO_2 and 10 mol% 1,4-dioxane. Temperatures of 50–140 °C and pressures of 70–80 bars were applied. The reactions were followed in time. The applied reaction times were 1, 2, 4, and 24 h. After the modification, the pressure was slowly released and the temperature was allowed to decrease to below 50 °C before opening the high-pressure cell in order to avoid discolouration of the granules by oxidation. The granules were washed with acetone and dried in a vacuum oven at 80 °C for 16 h under a nitrogen flow.

2.3. Characterisation of unmodified and modified PA-6

Both for unmodified and modified PA-6 samples, the end group concentrations, the relative viscosities, the number and weight average molecular weights (\bar{M}_n and \bar{M}_w) as well as the MWDs, and the melt viscosities were determined as described in detail in Part 1 of this series of papers [6]. Also the applied conditions for the DSC measurements, performed on these samples, were described in Part 1.

2.4. FTIR spectroscopy

FTIR spectra of thin slices (20 μm thick) cut from the middle of PA-6 granules were recorded on a Bio-Rad FTS 6000 spectrometer equipped with a microscope.

3. Results and discussion

3.1. Modification of the amine and carboxylic acid end groups of PA-6 granules with 1,2-epoxybutane in supercritical or subcritical media

1,2-Epoxybutane was used as blocking agent for the end groups of PA-6, since this compound is reactive towards both carboxylic acid and the amine groups [7,8]. Moreover, it is a relatively small compound, which is favourable for its impregnation into the swollen PA-6 granules. In Fig. 1 the reaction scheme is given for the modification of the amine and carboxylic acid end groups with 1,2-epoxybutane. One must keep in mind that both amine and carboxylic acid end groups of one polymer chain can be blocked, and that one amine end group is able to react with two molecules of 1,2-epoxybutane.

As discussed in Part 1 of this series of papers [6], the addition of 10 mol% 1,4-dioxane to CO₂ resulted in better blocking of the amine end groups of the PA-6, as a result of an increased polarity of the mixture and a better sorption of the mixture by the polymer granules. Most likely the addition of the polar 1,4-dioxane enhances the solubility of the blocking agent in the mixture as well. The modifications in SCFs were performed at 140 °C and 70 bars in propane/1,4-dioxane mixtures and at 100 or 140 °C and 80 bars in CO₂/1,4-dioxane mixtures. For reactions in the subcritical region, temperatures of 70 and 100 °C and a pressure of 70 bars were applied for propane/10 mol% 1,4-dioxane mixture, whereas for CO₂/10 mol% 1,4-dioxane mixtures, 50 °C and 80 bars were applied. By “subcritical” is meant that the

modifications are performed below the critical point, i.e. in homogeneous liquid mixtures of either propane or CO₂ with 1,4-dioxane.

When blocking the amine end groups with 1,2-epoxybutane, the primary amine groups are converted into secondary amine groups. These secondary amine groups cannot be distinguished from the original primary amine groups by standard titration experiments. Thus, no conclusions on blocking efficiency could be drawn from amine group concentrations determined by titration. We, therefore, focus attention on the blocking of the carboxylic acid end groups with titration measurements. Since, under similar conditions, epoxides are more reactive towards primary amines than towards carboxylic acids, it can be expected that the blocking of the amine groups is at least as efficient as the simultaneous blocking of the carboxylic acid groups.

In Fig. 2, the results of the carboxylic acid end group modification of PA-6 with 1,2-epoxybutane in supercritical or subcritical propane/10 mol% 1,4-dioxane are given. The carboxylic acid end group concentrations were determined on PA-6 powder, which was obtained by dissolving the granules in *m*-cresol and precipitating the polyamide in methanol. As discussed in Part 1 [6], the precipitation step is necessary to remove possible residual blocking agent, which might not have been removed completely upon releasing the pressure. To obtain a good reference material, the unmodified PA-6 was also dissolved in either *m*-cresol or TFE/CHCl₃ and precipitated in methanol. The amine and carboxylic acid end group concentrations and the relative viscosity of unmodified PA-6 granules and (dissolved and precipitated) powder are given in

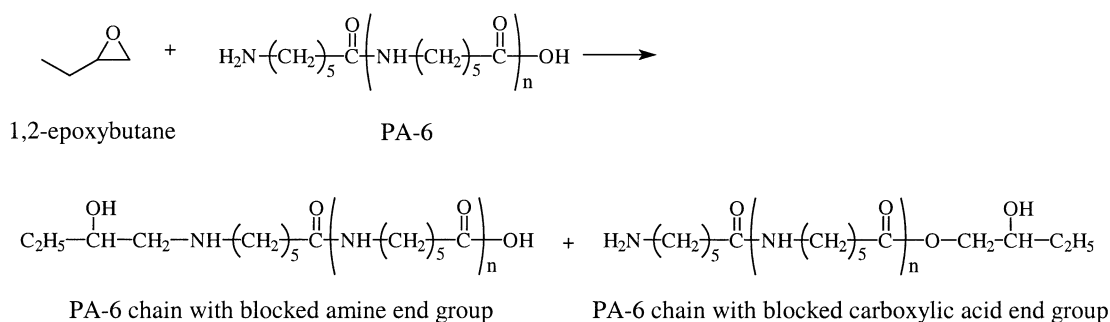


Fig. 1. Schematic representation of the amine and carboxylic acid end group modification of PA-6 with 1,2-epoxybutane.

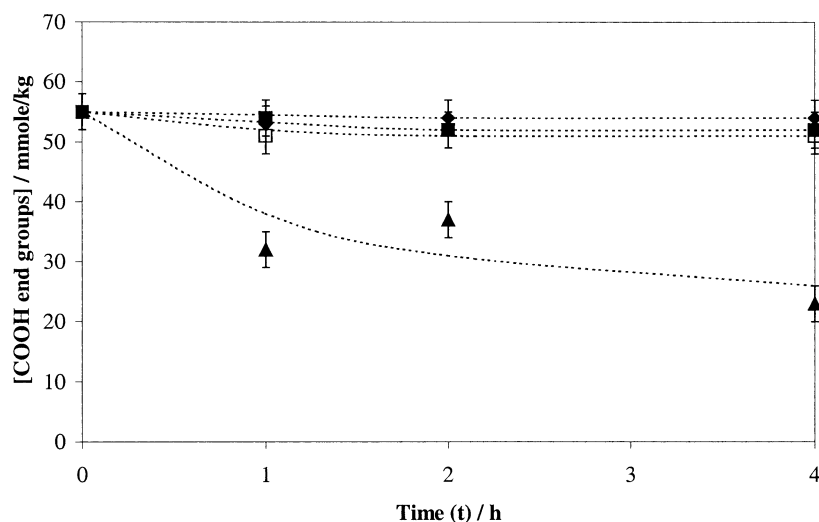


Fig. 2. Carboxylic acid end group modification of PA-6 with 1,2-epoxybutane in supercritical or subcritical propane/10 mol% 1,4-dioxane. -◆-: 70 °C, 70 bars, subcritical fluid; -□-: ref. exp., 100 °C, 70 bars, subcritical fluid; -■-: 100 °C, 70 bars, subcritical fluid; -▲-: 140 °C, 70 bars, sc fluid.

Table 1. From this table it is clear that purification of the sample by dissolving in *m*-cresol, followed by precipitation, raises the relative viscosity and decreases the amine end group concentration by 5 mmol/kg. This increase in relative viscosity and minor decrease in amine end group concentration is probably caused by extraction of low molecular weight oligomers.

The results for the modification of the carboxylic acid end groups in propane/10 mol% 1,4-dioxane, presented in Fig. 2, show that under subcritical conditions, i.e. at 70 and 100 °C, no reaction between the epoxide and the carboxylic acid end groups had occurred. Obviously, the fact that the concentration of 1,2-epoxybutane in propane/10 mol% 1,4-dioxane at 100 °C is higher than in propane/10 mol% 1,4-dioxane at 70 °C is of minor importance. (With increasing temperature, the concentration 1,2-epoxybutane in propane/10 mol% 1,4-dioxane increases since with increasing temperature, keeping the pressure

at a constant value of 70 bars, the density of the mixture decreases, resulting in a lower amount of propane/1,4-dioxane mixture present in the high pressure cell, while the total amount of 1,2-epoxybutane remains constant. This is the so-called concentration effect).

With increasing temperature from 100 °C (subcritical fluid) to 140 °C (SCF), the blocking of the carboxylic end groups improves. After 4 h, a decrease from 55 to 23 mmol/kg carboxylic acid end groups is found for the modification in supercritical propane/1,4-dioxane. The better modification is most likely the result of an increased reactivity of the 1,2-epoxybutane at 140 °C compared with 100 °C, which probably dominates the effect of going from subcritical to supercritical conditions (furtheron, where the results on the modification in CO₂/1,4-dioxane are discussed, we show that supercritical conditions at 100 °C are insufficient to

Table 1

Specifications of unmodified PA-6 granules and powder, precipitated from *m*-cresol or TFE/CHCl₃ (1:1 v/v) in methanol

PA-6	Granules	Precipitated from <i>m</i> -cresol	Precipitated from TFE/CHCl ₃
[NH ₂ end groups] (mmol/kg)	55 (±2)	50 (±2)	53 (±2)
[COOH end groups] (mmol/kg)	53 (±3)	55 (±3)	55 (±3)
Relative viscosity (η_{rel}) in 90 wt.% formic acid	2.47 (±0.02)	2.58 (±0.02)	2.49 (±0.02)

Table 2

Relative viscosity (η_{rel}) in 90% formic acid and discolouration of unmodified PA-6 and PA-6 modified with 1,2-epoxybutane for 4 h in subcritical and SCFs

Entry	Conditions	η_{rel} in 90% formic acid	Discolouration
1	PA-6 (unmodified)	2.58/2.47 ^a /2.49 ^b	— —
2	Subcritical propane/10 mol% 1,4-dioxane, 70 °C	2.56	— —
3	Reference, subcritical propane/10 mol% 1,4-dioxane, 100 °C	2.59	+
4	Subcritical propane/10 mol% 1,4-dioxane, 100 °C	2.53	— —
5	Reference, sc propane/10 mol% 1,4-dioxane, 140 °C	2.52 ^{a,c}	— —
6	Sc propane/10 mol% 1,4-dioxane, 140 °C	2.40/2.23 ^c	— —
7	Subcritical CO ₂ /10 mol% 1,4-dioxane, 50 °C	2.60	— —
8	Reference, scCO ₂ /10 mol% 1,4-dioxane, 100 °C	2.52	+ —
9	ScCO ₂ /10 mol% 1,4-dioxane, 100 °C	2.48 ^b	— —
10	Reference, scCO ₂ /10 mol% 1,4-dioxane, 140 °C	2.57/2.75 ^c /2.61 ^{a,c}	+ —
11	ScCO ₂ /10 mol% 1,4-dioxane, 140 °C	2.30	— —

Samples are precipitated from *m*-cresol unless indicated otherwise. Symbols for discolouration: +, yellow/brown; + —, light yellow; — —, white.

^a Granules (not precipitated).

^b Precipitated from TFE/CHCl₃.

^c 24 h reaction time instead of 4 h.

force the reaction between COOH end groups and 1,2-epoxybutane).

We have to keep in mind that, although the carboxylic acid end groups had not been modified at 70 and 100 °C, the much more reactive amine end groups might have been end capped by the 1,2-epoxybutane at these temperatures (see earlier).

In Table 2, the influence of the modifications on the relative viscosity (η_{rel} in formic acid) and the discolouration of the granules is given. “Reference” samples (Entries 3, 5, 8 and 10) are samples, which were kept in the high-pressure cell, under the conditions given in Table 2, to which no 1,2-epoxybutane had been added. This was done to study the effect of the sole supercritical or subcritical fluid on end group concentration, relative viscosity and discolouration.

As can be seen in Table 2 several relative viscosities decreased after modification. For Entry 6 the relative viscosity of polymer powder has decreased from 2.58 to 2.40, already after 4 h of modification in propane/1,4-dioxane at 140 °C. This large decrease was not observed for the modifications at 70 and 100 °C (Entries 2 and 4 in Table 2). One explanation for this decrease could be that the polymer had degraded at 140 °C (i.e. chain scission), resulting in the formation of more end groups, which subsequently can be blocked by the 1,2-epoxybutane. On the other hand it is possible that, due to the block-

ing of end groups, the interaction of the polymer molecules with the solvent, used for the solution viscosity measurements, and with that the relative viscosity, had changed. For some modified samples, this was checked by determining the MWDs of the polymers (see Section 3.2.). In that specific section the explanation for the viscosity drop will be given.

Looking at the discolouration of the granules, only the reference samples (i.e. granules without the addition of 1,2-epoxybutane) were discoloured, whereas the modified samples were not, which is an advantage of the modification of PA-6 with 1,2-epoxybutane in comparison with the modification with succinic anhydride (SA), described in Part 1 of this series of papers [6].

In Fig. 3 and Table 2 (Entries 7, 9 and 10), the results for the modification of the carboxylic acid end groups in CO₂/10 mol% 1,4-dioxane at 50, 100 and 140 °C are shown. The carboxylic acid end group concentrations and the relative viscosities were determined on dissolved and precipitated PA-6 powders.

The results show that under subcritical conditions, i.e. at 50 °C, hardly any reaction between the epoxide and the carboxylic acid end groups had occurred. Increasing the temperature to 100 °C, thereby bringing the CO₂/10 mol% 1,4-dioxane mixture into the supercritical state, does not result in a decrease in carboxylic acid end group concentration, despite the

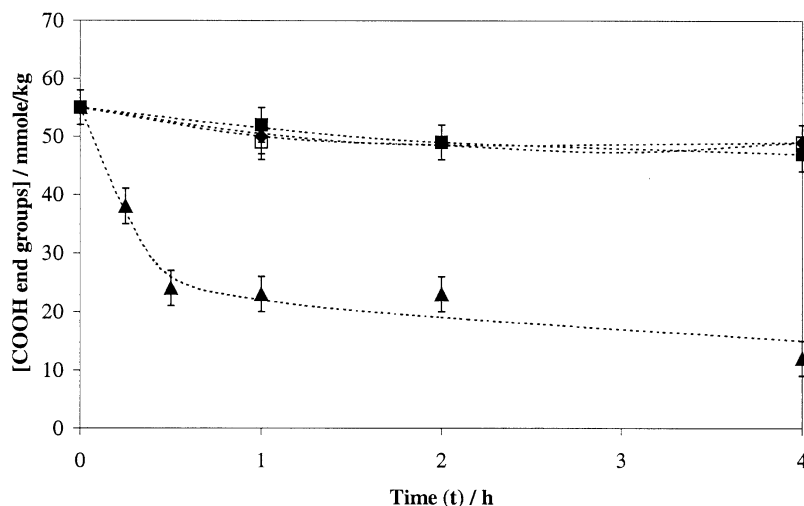


Fig. 3. Carboxylic acid end group modification of PA-6 with 1,2-epoxybutane in supercritical or subcritical CO₂/10 mol% 1,4-dioxane. -◆-: 50 °C, 80 bars, subcritical fluid; -□-: ref. Exp., 100 °C, 80 bars, sc fluid; -■-: 100 °C, 80 bars, sc fluid; -▲-: 140 °C, 80 bars, sc fluid.

concentration effect of 1,2-epoxybutane in CO₂/10 mol% 1,4-dioxane, which as described earlier for propane/1,4-dioxane mixtures increases with increasing temperature.

With increasing temperature from 100 to 140 °C, the blocking of the carboxylic end groups improves. In scCO₂/10 mol% 1,4-dioxane of 140 °C, already after 30 min a decrease from 55 to 24 mmol/kg carboxylic acid end groups is observed, implying effective blocking. The better modification is a result of an increased reactivity between the COOH end groups and 1,2-epoxybutane at 140 °C compared with 100 °C. The relative viscosity in formic acid for this modified PA-6 had decreased significantly (from 2.58 to 2.30). This decrease can be explained in terms of a different interaction of the polymer with the solvent, and is not related to chain scission (see Section 3.2). This large viscosity drop is not observed for the modification at 50 °C, and only a small viscosity drop is observed for the PA-6 modified at 100 °C (Entries 7 and 9 in Table 2), which is in agreement with the less efficient end capping at these lower temperatures. A preliminary conclusion from the CO₂/1,4-dioxane results might be that going from subcritical (a homogeneous liquid) to supercritical conditions (from 50 to 100 °C) is not enough to block the carboxylic acid end groups of PA-6. Not only a quick sorption of CO₂/1,4-dioxane containing 1,2-epoxybutane is needed (see results de-

scribed in Part 1 [6], Fig. 6), but also a temperature exceeding 100 °C is required to get the chemistry going.

For all modifications in CO₂/1,4-dioxane the granules did not discolour (see Table 2), contrary to the modification with SA described in Part 1 [6].

Now that we have shown that the 1,2-epoxybutane does react with the carboxylic acid end groups, it is of interest to check whether only the surface of the granules or also the core of the granules is modified, just like was done for the modifications of PA-6 granules with SA in Part 1 [6]. Therefore, from both a granule, which was modified in CO₂/1,4-dioxane at 140 °C for 4 h, and an unmodified granule, a cross section was cut and investigated with FTIR spectroscopy.

In Fig. 4 it is shown that extra, but weak absorptions for the modified PA-6 are found at 1725, 1121 and 874/cm compared with unmodified PA-6. The absorption peak at 1725/cm is ascribed to the new carbonyl groups, formed upon reaction of the acid end groups with the epoxide. The absorption peaks at 1121 and 874/cm are ascribed to the C–N and C–O vibrations of the formed secondary amines and alcohols, the latter being the result of both the reaction of NH₂ and COOH end groups with 1,2-epoxybutane (see Fig. 1).

Since there was no difference between the spectra for the surface and the core of the modified granule (a, b in Fig. 4), and since both spectra a and b differ from

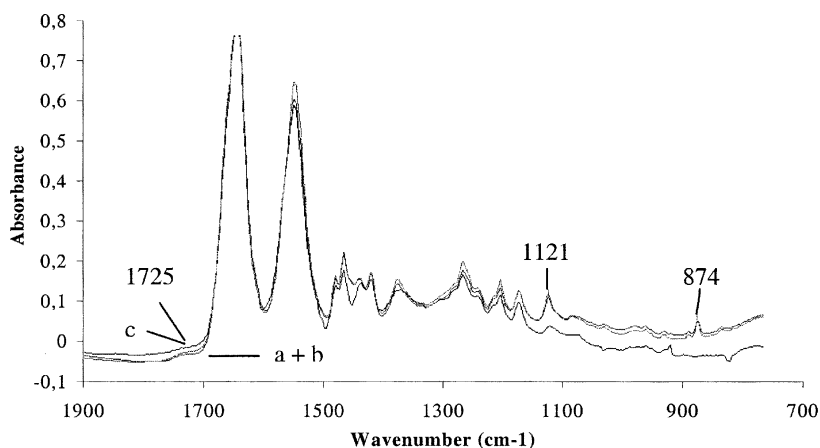


Fig. 4. FTIR spectra of a cross section of a PA-6 granule modified with 1,2-epoxybutane in scCO_2 /10 mol% 1,4-dioxane at 140°C for 4 h: a, surface; b, core; c, surface of an unmodified PA-6 granule.

the spectrum of the unmodified PA-6 (c in Fig. 4), it is concluded that the modification had occurred in a quite homogeneous way.

In Part 1 of this series of papers [6] it is discussed that CO_2 saturated with SA diffused slower into the PA-6 granules than pure CO_2 because of a reduction of the free volume after partial blocking of the chain ends. Furthermore, the slower diffusion may be explained by the fact that a more acidic polymer had been generated after the reactive SA had reacted with the amine end groups, forming amic acid end groups. Because the solubility of CO_2 in an acidic environment is worse than in a neutral or basic environment, the diffusion into the PA-6 granules is expected to be slower. The epoxide used in this paper is less reactive than the SA, resulting in a slower reduction of the free volume. Furthermore, upon reaction of the epoxide with both amine and carboxylic acid end groups, secondary alcohols are formed, which are more attractive for CO_2 than the formed amic acid groups in the case of SA modification.

To investigate the possible advantage of the supercritical technique over the modification in organic liquids, modifications were also performed in decane/10 mol% 1,4-dioxane at 100°C and in decaline/10 mol% diethylene glycol diethyl ether at 100 and 140°C . We realise that it is difficult to compare the modifications in SCFs with those in common liquids and draw hard conclusions, since not only the state of the reaction medium changes (liquid or sc), but also the reaction

medium itself (i.e. molecular size, polarity etc.). Diethylene glycol diethyl ether was chosen instead of 1,4-dioxane, since (1) its boiling point is 189°C and, therefore, it remains a liquid during the modification at 140°C and (2) it has a solvent polarity reasonably close to that of 1,4-dioxane (see also Section 3.4 of Part 1 [6]). In Fig. 5 the carboxylic acid end group concentration versus time is given for these experiments. The carboxylic acid end group concentration of the precipitated PA-6 powders decreased from 55 to 49 and to 40 mmol/kg after 4 h reaction time at respectively 100 and 140°C in decaline/10 mol% diethylene glycol diethyl ether. Although the end group modification at 140°C is somewhat more effective than at 100°C (because the reaction at 100°C is too slow), the modification is not as effective as in SCFs at 140°C . The carboxylic acid concentrations after 4 h at 140°C are 23 mmol/kg in propane/10 mol% 1,4-dioxane, 12 mmol/kg in CO_2 /10 mol% 1,4-dioxane and 40 mmol/kg in decaline/10 mol% diethylene glycol diethyl ether. Comparing the modifications at 100°C but in different solvent mixtures, the carboxylic acid end group concentrations are the same within the experimental error. Taking into account both the modifications with SA (Figure 12 in Part 1 [6]) and the liquid organic solvent modifications with 1,2-epoxybutane, the modifications in decane/10 mol% 1,4-dioxane are slightly more efficient than those in the corresponding decaline/diethylene glycol diethyl ether based mixtures. Since the 1,4-dioxane

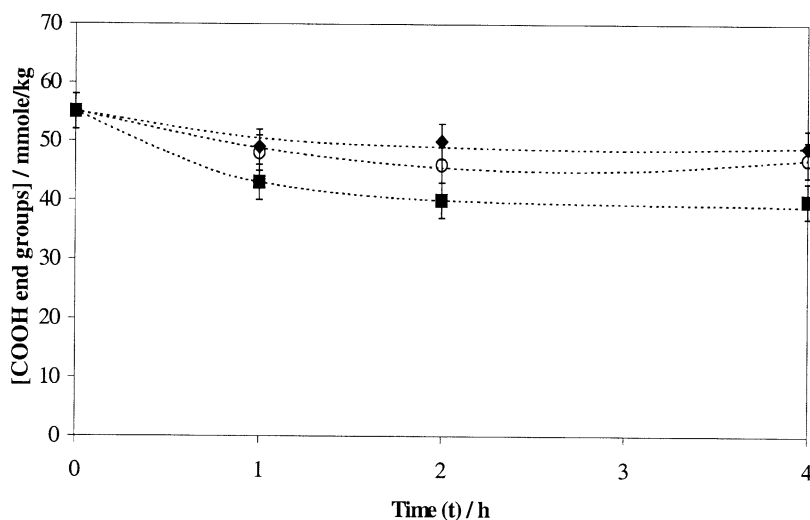


Fig. 5. Carboxylic acid end group modification of PA-6 with 1,2-epoxybutane in liquid organic solvent mixtures at atmospheric pressure; ◆-: decaline/10 mol% diethylene glycol diethyl ether, 100 °C; ○-: decane/10 mol% 1,4-dioxane, 100 °C; ■-: decaline/10 mol% diethylene glycol diethyl ether, 140 °C.

containing solvent mixture resembles the supercritical mixtures the most, we speculate that the modification in decane/10 mol% 1,4-dioxane at 140 °C would result in a slightly lower carboxylic acid end group concentration than observed for the same modification in decaline/10 mol% diethylene glycol diethyl ether at 140 °C (the latter resulting in a COOH concentration of 40 mmol/kg). So, a difference in blocking efficiency between liquids and sc fluids seems to exist in favour of the sc fluids. However, the advantage of using SCFs for polymer modification is less pronounced than expected.

In Table 3, the influence of the modifications in organic solvents on the relative viscosity (η_{rel} in

formic acid) and the discolouration of the granules are given. “Reference” samples (Entries 2 and 5) are samples, which were kept in the high-pressure cell under the conditions given in Table 3, to which no 1,2-epoxybutane had been added. As can be seen for Entry 3 and 4, the relative viscosity after 4 h of modification in the organic solvent at 100 °C did not decrease within the experimental error of ± 0.02 . This is not surprising since Fig. 5 showed that only a small amount of carboxylic acid end groups had been blocked. Surprising is that for modification in organic solvents at 140 °C (Entry 6) no decrease in relative viscosity is observed, whereas this was the case for the modifications at similar temperatures in SCF

Table 3

Relative viscosity (η_{rel}) in 90 wt.% formic acid and discolouration of unmodified PA-6 and PA-6 modified with 1,2-epoxybutane for 4 h in organic solvents

Entry	Conditions	η_{rel} in formic acid	Discolouration
1	PA-6 (unmodified)	2.58/2.47 ^a /2.49 ^b	— —
2	Reference, decaline/10 mol% diethylene glycol diethyl ether, 100 °C	2.50 ^b	+ —
3	Decaline/10 mol% diethylene glycol diethyl ether, 100 °C	2.58	— —
4	Decane/10 mol% 1,4-dioxane, 100 °C	2.61	— —
5	Reference, decaline/10 mol% diethylene glycol diethyl ether, 140 °C	2.54 ^b	+
6	Decaline/10 mol% diethylene glycol diethyl ether, 140 °C	2.57	+ —

Samples are precipitated from *m*-cresol. Symbols for discolouration: +, yellow/brown; + —, light yellow; — —, white.

^a Granules (not precipitated).

^b Precipitated from TFE/CHCl₃.

Table 4
Results of SEC measurements in HFIP on unmodified and modified PA-6

Entry	Materials	\bar{M}_w (kg/mol)	\bar{M}_w/\bar{M}_n
1	Unmodified PA-6, granules	23	2.3
2	Unmodified PA-6, precipitated from <i>m</i> -cresol	25	2.2
3	Unmodified PA-6, precipitated from TFE/CHCl ₃	26	2.2
4	Sample 3 and subsequent treatment of 30 min at 260 °C	64	3.2
5	PA-6 modified in propane/10 mol% 1,4-dioxane, 100 °C, 4 h and precipitated from <i>m</i> -cresol	25	2.0
6	Sample 5 and subsequent treatment of 30 min at 260 °C	29	2.7
7	PA-6 modified in CO ₂ /10 mol% 1,4-dioxane, 140 °C, 4 h and precipitated from <i>m</i> -cresol	25	2.0
8	Sample 7 and subsequent treatment of 30 min at 260 °C	35	2.3

mixtures. Polymers with a similar molecular weight, but with different end groups exhibit a different interaction with the solvent ([6], see also Section 3.2). We, therefore, expected at least a slight decrease in relative viscosity after the modification at 140 °C in organic solvents, since the carboxylic acid end group concentration decreased from 55 to 40 mmol/kg. Obviously, the change in carboxylic acid end group concentration is too small to result in a significantly different interaction with the solvent.

In summary, when comparing the results of the PA-6 modifications in organic solvent mixtures at 140 °C with those of the modification in sc propane/10 mol% 1,4-dioxane (Fig. 2) and scCO₂/10 mol% 1,4-dioxane (Fig. 3) better results were obtained for the modification in SCFs, provided that the temperature was high enough to let the carboxylic acid end groups react with the epoxy groups. Furthermore, the PA-6 modifications in propane/1,4-dioxane and CO₂/1,4-dioxane with 1,2-epoxybutane did not result in discoloured granules (see Table 2), contrary to the modification of PA-6 with SA described in Part 1 [6].

3.2. Molecular weight distribution of modified and unmodified PA-6

In Table 2, the relative viscosity and a qualitative indication for the discolouration of the granules after 4 h of modification in subcritical and SCFs are given. As was mentioned in the previous section, merely a change in end group concentration can influence the value found for the relative viscosity. As shown in Table 2, decreases in relative viscosity were found, particularly for PA-6 samples, which were modified at 140 °C. However, a decrease in relative viscosity does not necessarily imply a decrease in molec-

ular weight, which e.g. could have been caused by chain scission of the polymer. The interaction of the polymer with the solvent, which directly determines the relative solution viscosity, can change when the end groups are changed, i.e. the relative viscosity can change when the end groups are blocked [6]. Therefore, some of these modified PA-6 samples were subjected to SEC measurements to determine MWD and molecular weights (\bar{M}_w) before and after modification (Table 4 and Fig. 6).

The unmodified PA-6 samples, which were dissolved and precipitated from *m*-cresol or TFE/CHCl₃ (Entries 2 and 3), show an increased molecular weight (\bar{M}_w) compared with the unmodified PA-6 granules (Entry 1). This is not surprising, since low molecular weight oligomers are washed away during the precipitation step. Comparing the MWDs of modified PA-6 with unmodified PA-6 (compare Entries 5 and 7 with Entry 2 of Table 4) it turns out that the molecular weight of PA-6, modified in either propane/1,4-dioxane at 100 °C or in CO₂ 1,4-dioxane at 140 °C, remains constant. Before and after the treatment with 1,2-epoxybutane the weight average molecular weights are 25 kg/mol. Therefore, the decrease in relative viscosity, from 2.58 to 2.53 (Entry 4, Table 2), respectively, to 2.30 (Entry 11, Table 2), does not imply a change in molecular weight, but a different interaction of the polymer with the solvent used for the determination of the relative viscosity. The increased \bar{M}_w obtained for unmodified PA-6, precipitated from TFE/CHCl₃, which was used in melt viscosity measurements (\bar{M}_w is 64 instead of 26 kg/mol, Entries 3 and 4, Table 4), is ascribed to the post condensation reaction, which occurs between the amine and carboxylic acid end groups at 260 °C. This post condensation reaction, and therewith an

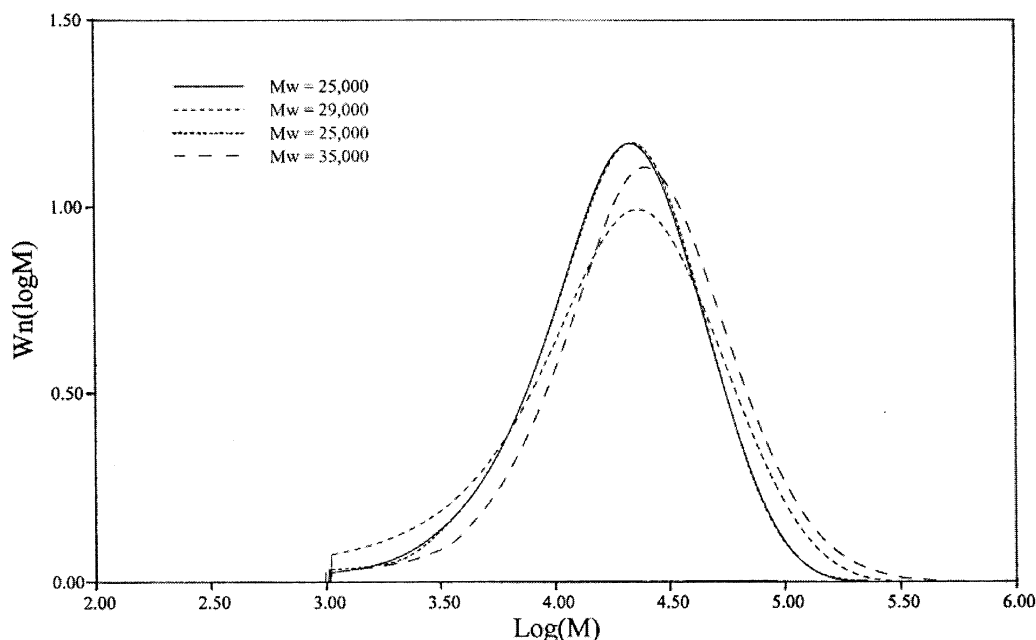


Fig. 6. SEC/DV Chromatogram of PA-6 modified in propane/10 mol% 1,4-dioxane, 100 °C, 4 h (—); PA-6 modified in propane/10 mol% 1,4-dioxane, 100 °C, 4 h and subsequent treatment of 30 min at 260 °C (---); PA-6 modified in CO₂/10 mol% 1,4-dioxane, 140 °C, 4 h (···); PA-6 modified in CO₂/10 mol% 1,4-dioxane, 140 °C, 4 h and subsequent treatment of 30 min at 260 °C (— · —).

enhanced molecular weight, which can be expected for unmodified PA-6 in the melt, should be absent or at least limited for polyamides of which the end groups have partially been blocked. Indeed the PA-6 samples, either modified in propane/1,4-dioxane at 100 °C or in CO₂/1,4-dioxane at 140 °C, show relatively small increases in \bar{M}_w upon melting. Increases from 25 to 29 kg/mol (Entry 6, Table 4) and from 25 to 35 kg/mol (Entry 8 Table 4 and Fig. 6) were found, respectively. These results clearly point to an increased melt stability of the PA-6 (see also Section 3.4), which was one of the aims of this work.

3.3. Differential scanning calorimetry (DSC)

To check whether the end group modification might have a nucleating effect on the crystallisation behaviour of the polymer, one modified sample was molten, recrystallised and compared with the unmodified PA-6, the ‘precursor’ polymer (Table 5). Looking at the DSC results in Table 5, it is clear that the melt and crystallisation behaviour of the modified

PA-6 is similar to that of unmodified PA-6. The differences in melting points (both $T_{m,1}$ and $T_{m,2}$), the degrees of crystallinity ($\Delta H_{fus,1}$ and $\Delta H_{fus,2}$) and the crystallisation temperatures (T_c) are only marginal.

A nucleating effect (caused by the formation of new end groups) would result in a higher T_c , which is not the case here, although the modified end groups look different from the unmodified end groups, and, therefore, might cluster in the melt and cause some pre-orientation of the polymer molecules, as described in literature for e.g. polyimides [9]. For the modification of the end groups with SA (Part 1, [6]) an increased T_c was observed, partially caused by a nucleating effect and partially by a decrease in molecular weight. Here, no decrease in molecular weight was found (Table 4, Entries 2 and 7).

3.4. Melt stability of modified and unmodified PA-6

In the previous section it was shown that modified samples after treatment at 260 °C for 30 min show a relatively small increase in molecular weight com-

Table 5

Results of DSC measurements of unmodified PA-6 and PA-6 modified with 1,2-epoxybutane in scCO₂/10 mol% 1,4-dioxane at 140 °C and 80 bars for 24 h

Entry	Conditions of modification	$T_{m,1}$ (°C)	$\Delta H_{fus,1}$ (J/g)	$T_{m,2}$ (°C)	$\Delta H_{fus,2}$ (J/g)	T_c (°C)
1	Unmodified PA-6	224	89	223	66	177
2	Modified PA-6	224	82	224	65	179

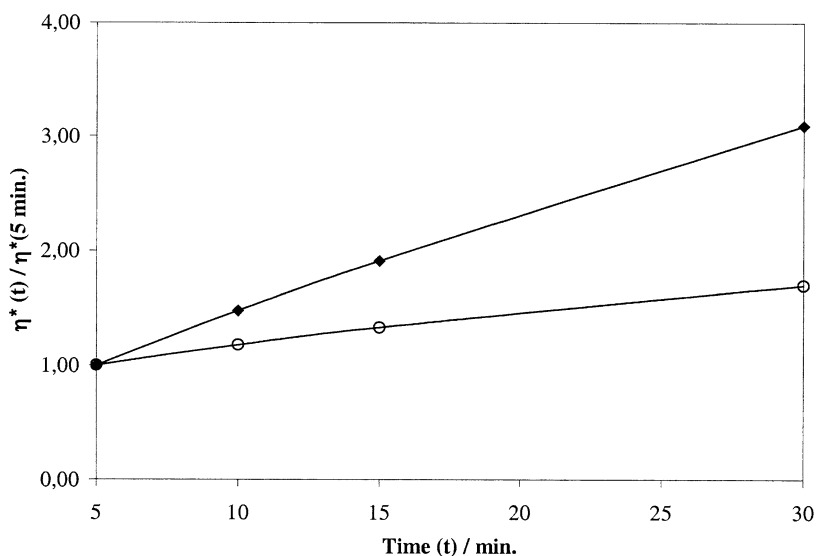


Fig. 7. Melt stability vs. time of unmodified PA-6 (—◆—) and PA-6 modified with 1,2-epoxybutane in propane/10 mol% 1,4-dioxane at 100 °C and 70 bars (—○—).

pared with the unmodified PA-6 after the same treatment. To confirm that the modification of PA-6 with 1,2-epoxybutane has a positive effect on the melt stability, rheology measurements were performed on the most promising modified PA-6 sample with respect to molecular weight, relative viscosity, discolouration, and end group concentration.

In Fig. 7 the influence on the melt stability of the modification of PA-6 in subcritical propane/10 mol% 1,4-dioxane at 100 °C with 1,2-epoxybutane is shown. For $\omega = 1$ rad/s the relative complex viscosity $\eta^*(t)/\eta^*$ (5 min) is plotted versus the residence time in the melt. This figure shows a significantly improved melt stability for the modified PA-6 sample compared with the unmodified PA-6. At first sight this seems a surprising result, since the carboxylic end groups were hardly blocked (see Fig. 2). Obviously, at this temperature the more reactive amine end groups are capable of reacting with the epoxide, in contrast with the

carboxylic acid end groups. This indicates that the blocking of the amine end groups must be responsible (and is obviously sufficient) for the improved melt stability.

4. Conclusions

In this work it was shown that it is possible to block the carboxylic acid end groups, present in PA-6 granules, with 1,2-epoxybutane in supercritical and subcritical fluids. It was found that better blocking of the carboxylic acid end groups is realised at higher temperatures. However, after modification at higher temperatures, a decrease in relative viscosity was found. SEC measurements showed that this decrease in relative viscosity not necessarily implies that chain scission had occurred, but that it must be ascribed to a different interaction of the end capped

macromolecules with the solvent in which the relative viscosity is determined.

For the melt stabilities of the modified PA-6, satisfying results were obtained upon modification of PA-6 in subcritical propane/10 mol% 1,4-dioxane at 100 °C. An improved melt stability was obtained without discolouration of the PA-6 granules, thanks to the blocking of the amine end groups but leaving the majority of the carboxylic acid end groups unblocked.

Overall, it can be concluded that the end group modification of solid PA-6 particles with 1,2-epoxybutane in subcritical propane/1,4-dioxane at 100 °C is optimum, if all relevant aspects like the decrease in end groups after modification, the molecular weight stability, the colour stability, and the improved melt stability are taken into account. With respect to the PA-6 end group modification with SA described in Part 1 of this series of papers [6], the modification with 1,2-epoxybutane is preferred, since no discolouration occurred, and the 1,2-epoxybutane is less reactive than SA, which is favourable for the diffusion of the blocking agent up to the core of the granules. In this way a rather homogeneous modification of the granules is realised.

Acknowledgements

We thank The European Community and DSM Research for financial support for this part of BRITE/EURAM project BE97-4520. We thank J. Haan, H. Govaers, J. ten Haaf, E. Bijleveld, N. Meijerink and

M. Rooijmans of the analysis departments. Finally, A. van Geenen, and M. van Duin are acknowledged for valuable discussions.

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