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Carboxylic acid end group modification of poly(butylene terephalate) in supercritical fluids

J.M. de Gooijer[a], M. Scheltus[b], M.A.G. Jansen[a], C.E. Koning[a,*]

[a]*Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b]*DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands*

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Abstract

Carboxylic acid end groups of poly(butylene terephalate) (PBT) granules were modified with an excess of 1,2-epoxybutane in supercritical CO_2 and in supercritical and subcritical mixtures of CO_2 with 10 mol% 1,4-dioxane. Temperatures of 120 and 180 °C and pressures of 60, 150 and 300 bar were applied. Best results were obtained for the modification in $scCO_2$ containing 10 mol% 1,4-dioxane at 180 °C. The carboxylic acid end group concentration was reduced from 44 mmol/kg to approximately 10 mmol/kg, which resulted in a significantly enhanced hydrolytic stability. This was demonstrated by measuring, both for unmodified and for 1,2-epoxybutane blocked PBT, the intrinsic viscosity as a function of hydrolysis time as well as the number and weight average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) before and after hydrolysis. After the modification, some PBT granules appeared more brittle than the unmodified PBT granules. The crystallinity proved to be enhanced by the plasticising effect of CO_2/1,4-dioxane at 180 °C. No indications were obtained that the 1,2-epoxybutane modified end groups exhibit a nucleating effect on the PBT crystallisation.

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1. Introduction

One of the many applications of poly(butylene terephthalate) (PBT) is optical fibre tubing. These fibre tubes are buried in the ground, and to ensure durability the polymer should be hydrolytically stable. However, the hydrolytic stability of PBT is not optimal and should be improved. The ability of carboxylic acid end groups to catalyse the hydrolysis of the ester bonds of poly(ethylene terephthalate) (PET), was investigated by Buxbaum [1] and several other researchers [2,3]. This hydrolysis is an auto-catalytic process, which implies that every time an ester functionality is hydrolysed, a new carboxylic acid end group is formed which further accelerates the hydrolysis process. By reducing the number of carboxylic acid end groups the hydrolysis can be retarded. Currently, people are trying to reduce the carboxylic acid end group concentration by changing the polymerisation process conditions, e.g. by changing pressure and temperature, or by adding a polymerisation co-catalyst.

A new and clean route, resulting in the carboxylic acid end group reduction of PBT, is the chemical modification of these end groups with reactive blocking agents in supercritical fluids. Supercritical CO_2 is frequently used as a medium for dyeing of polyester fibres [4–6], because it is non-toxic, non-flammable, inexpensive and environmentally benign [7]. The dye molecules are transported by the CO_2 molecules into the swollen polymer particles, where they are physically or chemically bound. Chemically modifying the carboxylic acid end groups of PBT in supercritical CO_2 is therefore a logical step, with good commercial perspectives. Some years ago, Buback et al. [8] reported the modification of side groups of ethylene-based copolymers in supercritical ammonia and near-critical water, but to the best of our knowledge the current paper for the first time describes the chemical modification of end groups of step-growth polymers in supercritical fluids.

Supercritical fluids do not dissolve the polyester but do have the possibility to swell the amorphous phase of the polymer. This is possible at relatively mild conditions,

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[*] Corresponding author. Tel.: +31-40-2472840; fax: +31-40-2473966.
E-mail address: c.e.koning@tue.nl (C.E. Koning).

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which might to a large extent limit undesired side reactions or degradation reactions, possibly occurring during modification in the melt. The hydrolysis of ester functionalities of PBT takes place in the amorphous phase, and it is important to block most of the carboxylic acid end groups, which are in this amorphous phase as well. When the PBT granules are swollen by a supercritical fluid, the blocking agent, which is dissolved in the fluid, can diffuse more easily into the amorphous phase of the granules. In this way significant amounts of carboxylic acid end groups are expected to be blocked in a relatively short time.

The swellability of the polymer depends on the interaction of the supercritical fluid with the polymer and on the crystallinity of the polymer. The higher the crystallinity, the more difficult it is to swell the polyester. This was observed by Von Schnitzler et al. [9]. They investigated the swelling of PET by CO_2. They found that the swelling of PET, with a crystallinity of about 33%, increased with increasing pressure and temperature, but only reached a maximum swelling of 5% v/v. Muth et al. [10] studied the modification of different polymers by impregnation of monomers and concluded that the sorption of CO_2 in poly(tetrafluoro ethylene) (PTFE) was low because of the high crystallinity of the polymer.

The crystallinity of the semi-crystalline PBT, used in this paper, is approximately 40%, depending on the applied processing conditions. Since this PBT has an even higher crystallinity than the PET mentioned above, and since sorption of CO_2 only occurs by the amorphous phase, the swelling of PBT by CO_2 and the sorption of CO_2, in view of the similarity of the chemical structure of PET and PBT, are expected to lie in the range of 2 to 5 wt%. In other words, the solubility of CO_2 in PBT is expected to be poor. However, if nevertheless low concentrations of carboxylic acid end groups can be reached, the supercritical fluid modification technique still proves to be useful.

It is the aim of this paper to study the scope and limitations of using supercritical CO_2 as a medium for the chemical modification of the carboxylic acid end groups of PBT with 1,2-epoxybutane.

2. Experimental

2.1. Materials

Poly(butylene terephthalate) (PBT) granules with $\bar{M}_n = 16,200$ g/mol (accurately determined based on the end groups) a carboxylic acid end group concentration of 44 ± 2 mmol/kg, and a relative viscosity in *m*-cresol (η_{rel}) of 1.84 ± 0.02 were kindly supplied by DSM Research, the Netherlands. 1,2-Epoxybutane (Aldrich), 1,4-dioxane (Acros Organics), and *m*-cresol (Merck) were used as received. High-purity CO_2 (4.5) was purchased from Hoekloos. All chemicals used were of analytical grade and used as received.

2.2. Selection of most suitable polar additive for CO_2

PBT granules and an excess of 1,2-epoxybutane (a 10-fold excess based on the carboxylic acid end group concentration of PBT) were stirred in mixtures of decaline with 10 mol% of a polar additive at 180 °C in a closed system for 4 h. The pressure of the system at 180 °C was estimated by taking the sum of the partial vapour pressures of decaline, 1,2-epoxybutane and the polar additive. For all systems the pressure was approximately 2 bar. Acetone, 1,4-dioxane and THF were chosen as the polar additives. The end group concentrations of all modified PBT samples were determined by titration (see Section 2.4). The polar additive, of which the addition to CO_2 resulted in the most pronounced decrease of the carboxylic acid end group concentration of the PBT, was used as a polar CO_2-additive for modifications in supercritical fluid mixtures.

2.3. Chemical modification of PBT with 1,2-epoxybutane in supercritical or subcritical media

Approximately 15 g of granules of poly(butylene terephthalate) (PBT) and 0.48 g of 1,2-epoxybutane (a 10-fold excess based on the carboxylic acid end group concentration of PBT) were placed in a 50 ml high-pressure cell (max. temperature = 200 °C, max. pressure = 850 bar). A mixture of CO_2 and 1,4-dioxane was prepared in a cylinder. Hereto, a calculated amount of 1,4-dioxane was transferred into the cylinder, after which the amount of CO_2, required to obtain a 10 mol% (18.2 wt%) concentration of 1,4-dioxane in CO_2, was transferred into the cylinder. The exact amounts were determined by weighing. After closing the cell containing the granules, the liquid CO_2 or the liquid mixture of CO_2 with 10 mol% 1,4-dioxane was pumped into the high pressure cell using a syringe pump. The desired pressure and temperature were obtained by increasing the temperature and subsequently increasing the amount of liquid, which resulted in the desired pressure. Temperatures of 120 and 180 °C and pressures of 60, 150 and 300 bar were applied. The reactions were performed during 1, 2, 4 and 24 h. After the modification, the non-reacted 1,2-epoxybutane was extracted from the PBT granules with epoxide-free supercritical fluid of the same composition as the fluid, which had been used during modification. It was checked whether or not the extraction of non-reacted 1,2-epoxybutane was complete (see Section 2.4). Subsequently, the pressure was slowly released and the temperature was allowed to decrease to room temperature before the cell was opened. The polymer granules were collected and were washed several times with acetone to remove the excess of blocking agent and 1,4-dioxane, which had remained as a thin liquid film on the surface of the granules. Then the granules were dried in a vacuum oven at 105–110 °C during 16 h under a nitrogen flow.

2.4. Characterisation of unmodified and modified PBT

The carboxylic acid end group concentrations of unmodified and modified PBT granules were determined by titration. Hereto, approximately 0.8 g (with 0.1 mg accuracy) of the PBT granules was dissolved in *o*-cresol. After dilution with chloroform, a photometric titration was performed with potassium hydroxide using bromocresol green as the indicator. To make sure that the residual blocking agent has indeed been removed after the extraction, washing and drying steps, a few samples were dissolved in hexafluoroisopropanol (HFIP) and precipitated in methyl *tert*-butyl ether (MTBE) (it might be that residual traces of blocking agent and 1,4-dioxane affect the measured COOH end group concentration). The obtained white precipitate was dried for 16 h at 105–110 °C in vacuum and under a nitrogen flow. The carboxylic acid end group concentrations of these PBT powders were determined in the same way as ascribed above.

2.5. Determination of the relative and intrinsic viscosity of PBT

Dried PBT samples were dissolved in *m*-cresol to obtain a polymer solution with concentration of approximately 1 g/dl (with 0.1 mg accuracy). The flow times of the polymer solution and the *m*-cresol were measured using an Ubbelohde suspended level viscometer.

2.6. Hydrolysis of unmodified and modified PBT

To determine the effect of carboxylic acid end group modification on the hydrolytic stability of PBT, unmodified and modified PBT granules were placed in water of 90 °C for a certain time. Subsequently, the samples were dried in a vacuum oven at 105–110 °C for 16 h. The relative and intrinsic viscosities of the PBT samples were determined as described in Section 2.5. The samples used for determining the influence of end group modification on the hydrolytic stability were unmodified PBT, and PBT samples modified for 24 h in (1) $scCO_2$ at 180 °C and 300 bar, (2) $scCO_2$ with 10 mol% 1,4-dioxane at 180 °C and 300 bar and (3) $scCO_2$ with 10 mol% 1,4-dioxane at 180 °C and 150 bar.

2.7. Size exclusion chromatography (SEC)

The number and weight average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) as well as the molecular weight distributions were determined using a modular size exclusion chromatograph (Waters 510 pump, Waters 710 auto injector, Spark Holland Mistral column oven, Waters 490 UV detector) equipped with two PFG linearXL columns from PSS (8 × 300 mm each, 7 μm particles). The eluent used was 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) containing 0.4 wt% ammonium acetate. Sample concentration was about 3 g/l, injection volume 50 μl, UV detector wavelength for the PBT samples was 265 nm.

A relative Polystyrene calibration curve, valid for THF solutions, was applied directly to the molecular mass calculations of the polyester samples, analysed in HFIP. The obtained ($\bar{M}_n$ and $\bar{M}_w$) values using this method were divided by a factor 2.8. This factor was based on a PBT sample with exactly known number average molecular weight, determined from the total number of end groups (data obtained from DSM Research, The Netherlands).

2.8. Differential scanning calorimetry (DSC)

A Perkin–Elmer differential scanning calorimeter (type Thermal Analysis, Pyris) was used to investigate the crystallinity of modified and unmodified PBT samples. From the two unmodified samples a thin slice from the middle of a granule (cross-section) was cut off and used for the DSC measurements (see Fig. 1). Three modified granular samples were ground and the powder was used for the DSC measurements. All samples were carefully dried before the measurements to limit as much as possible the hydrolytic degradation during heating. The samples were measured in the temperature range from 50 to 260 °C with a heating rate of 10 °C/min. The area of the melting peak (around 225 °C) was taken as a measure for the crystallinity.

3. Results and discussion

3.1. Selection of most suitable polar additive for CO_2

Polar additives (frequently called modifiers) are quite often added to supercritical fluids to improve the solubility of the reactants (here 1,2-epoxybutane) or extractants, and to enhance the swellability of the PBT granules. As described in Section 2, by performing model reactions in decaline, the most suitable additive for CO_2 was selected. The addition of 10 mol% 1,4-dioxane to the apolar decaline, in which the PBT granules were submerged, resulted in the most pronounced reduction of the number of carboxylic acid end groups of the PBT. Therefore this additive was selected as the polar additive for the carboxylic acid end group modification in supercritical and subcritical CO_2.

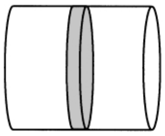

Fig. 1. Schematic representation of a PBT granule. The cross-section used for the DSC analysis is depicted in grey.

3.2. Chemical modification of PBT with 1,2-epoxybutane in supercritical or subcritical media

In our investigation into the chemical modification of swollen polymer particles in supercritical fluids, PBT with 44 mmol/kg carboxylic acid end groups was modified with 1,2-epoxybutane in supercritical CO_2 or in a supercritical or subcritical mixture of CO_2 with 10 mol% 1,4-dioxane. The critical pressures (P_c) and temperatures (T_c) of CO_2 and 1,4-dioxane [11,12], and calculated values for P_c and T_c using Kay's rule [13] for mixtures of CO_2 with 10 mol% 1,4-dioxane, are given in Table 1.

Temperatures of 120 and 180 °C and pressures of 60, 150 and 300 bar were applied. The reactions were performed during 1, 2, 4 and 24 h. The modification at a pressure of 60 bar (subcritical conditions, i.e. both CO_2 and 1,4-dioxane are in the gas phase) was chosen in order to be able to trace possible differences between supercritical and subcritical conditions. The advantage of both subcritical modification in the gas phase and supercritical modification, compared to melt or solution modification, is that milder reaction conditions can be applied and that residual solvent is more easily removed. The reaction temperature needs to be above the T_g of the PBT granules but below the T_m. It is crucial that the temperature is above the T_g in order to ensure sufficient chain mobility for the chemical modification to take place. Being below the T_m is important, since then the granules only swell and, after depressurisation, regain their original form and their free flowing character without sticking together. Therefore, after performing the desired chemistry, it is easy to collect the modified granules from the reactor. The chemistry of the modification of the carboxylic acid end groups with 1,2-epoxybutane is given schematically in Fig. 2. For the sake of clarity, unsaturated butenyl end groups, generated by an internal ester group pyrolysis at elevated temperatures, and always present in PBT to a certain extend, are omitted in Fig. 2.

We have to keep in mind that the hydroxyl end groups might also react with 1,2-epoxybutane, although carboxylic acid groups are expected to be much more reactive than hydroxyl functions, namely by a factor 10 to 20 [14]. The formed secondary hydroxyl groups are even less likely to react with 1,2-epoxybutane.

To prevent major hydrolysis of the main chain ester functionality in the polymer, which would result in chain scission and accordingly in worse mechanical properties, blocking of the carboxylic acid end group is necessary, since the acid end group is a catalyst for the hydrolysis process. When hydrolysis takes place new carboxylic acid end groups are formed, which further accelerate the hydrolysis process. When decreasing the carboxylic acid end group concentration from 44 mmol/kg to around or below 10 mmol/kg, the hydrolysis process is drastically diminished [15].

Table 1
Critical pressures (P_c) and temperatures (T_c) of CO_2, and 1,4-dioxane and calculated values using Kay's rule for P_c and T_c for mixtures of CO_2 with 10 mol% 1,4-dioxane

Fluid	P_c (bar)	T_c (°C)
CO_2	73.8	31.1
1,4-dioxane	52.1	313.9
CO_2/10 mol% 1,4-dioxane	71.7	59.3

Before discussing the carboxylic acid end group concentrations found for PBT granules, we first have to make sure that we are measuring the right concentrations. As was mentioned in Section 2.4, it might be that residual traces of blocking agent and 1,4-dioxane affect the measurement of the carboxylic acid end group concentration. To make sure that the residual blocking agent has indeed been removed after the modification and extraction, a few modified samples were dissolved and precipitated. The carboxylic acid end group concentrations and relative viscosities of the precipitated samples were then determined and compared with the corresponding values of the granules (Table 2).

PBT starting material was also precipitated, to make sure that there is no effect of the precipitating step itself on the determination of the carboxylic acid end group concentrations and relative viscosities.

Comparing all carboxylic acid end group concentrations of PBT granules with the corresponding PBT samples, which were dissolved and precipitated (Table 2), no difference in concentrations were found, taking into account the experimental error. In addition, the relative viscosities of the PBT samples did not change within the experimental error upon precipitation. From these results, we conclude that the extraction of non-reacted 1,2-epoxybutane and residual traces of 1,4-dioxane was complete. Therefore, we could determine the end group concentrations and the relative viscosities on PBT granules, saving an additional dissolving and precipitation step.

When looking at the relative viscosities of the modified PBT samples, with low carboxylic acid end group concentrations (entries 3–5, Table 2), decreased relative viscosities were found with respect to the viscosity of unmodified PBT (entry 1, Table 2). This could possibly be explained both in terms of a changed interaction of the polymer chain ends with the solution, and/or by a decrease in molecular weight as a result of chain scission of the polymer. In Section 3.4 we will come back to this point, and further details will be given concerning the relation between relative viscosities and molecular weights.

In Fig. 3, the carboxylic acid end group concentrations of PBT samples, which were modified with 1,2-epoxybutane under several conditions, are given versus modification time (experimental error is ±2 mmol/kg).

Comparing the results of the modification of the carboxylic acid end groups with 1,2-epoxybutane in $scCO_2$ at 120 °C (–◆–) and at 180 °C (–■–), learns that at 120 °C hardly any end groups are blocked, whereas, at

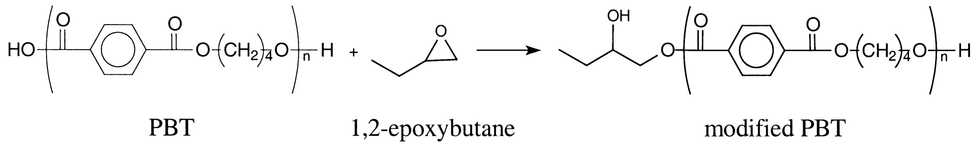

Fig. 2. Reaction scheme of the carboxylic acid end group modification of PBT.

180 °C blocking of the carboxylic acid end groups occurs rapidly. This is explained in terms of reactivity: at 120 °C, the 1,2-epoxybutane is not reactive enough towards the carboxylic acid end groups in the polymer. Some other researchers also observed that the curing of COOH containing powder coatings with multifunctional epoxides, in the presence of a catalyst, occurs readily at 180 °C or higher temperatures, and found that almost no curing takes place at lower temperatures [16]. Therefore, a temperature of 180 °C was chosen for further modification experiments. Carrying out the experiments at this temperature has two additional advantages: (1) better swelling of the granules with increasing temperature and therewith improved transportation of the supercritical fluid and the blocking agent into the granules, and (2) increased chain mobility in the amorphous phase of the polymer, resulting in a faster blocking of the carboxylic acid end groups. The effect of the increased chain mobility on the end group modification, however, is not expected to be large, since a temperature of 120 °C is already 80 °C above the T_g, which results already in an increased chain mobility. In addition, the supercritical fluid acts as a plasticiser, resulting in a decreased T_g.

At 180 °C and 300 bar in $scCO_2$, after 2 h a decrease from 44 to 26 mmol/kg carboxylic acid end groups is observed, and after 24 h a decrease to even 13 mmol/kg carboxylic acid end groups is obtained, which is close to the desired concentration of ca. 10 mmol/kg [15].

Comparing the results of the modification of the carboxylic acid end groups with 1,2-epoxybutane in $scCO_2$ (–■–) and $scCO_2$/1,4-dioxane (–▲–) at 180 °C and 300 bar, shows that the modification proceeds better in the $scCO_2$/1,4-dioxane mixture, although the difference is relatively small. A better modification in the $scCO_2$/1,4-dioxane mixture could be expected since in earlier work it was reported that adding a polar additive to the non-polar CO_2 increases its interaction with polymers containing hetero-atoms in their main chain. This would result in better sorption of the $scCO_2$/1,4-dioxane mixture, and therewith the blocking agent, by the polymer [17].

After 24 h modification in $scCO_2$/1,4-dioxane at 180 °C and 300 bar (–▲–) a concentration of 9 mmol/kg carboxylic acid end groups is obtained, which is below the target value of 10 mmol/kg. To investigate the effect of decreasing the pressure to below the critical pressure of the CO_2/1,4-dioxane mixture, additional modifications were performed at 150 and 60 bar, the latter resulting in a subcritical medium. Decreasing the pressure is accomplished by pressing a smaller amount of CO_2/1,4-dioxane into the high-pressure cell. Therefore, the CO_2/1,4-dioxane density decreases as well, which results in a higher concentration of the fixed amount of 1,2-epoxybutane in the medium with decreasing pressure. At 300 bar the concentration of 1,2-epoxybutane in CO_2/1,4-dioxane is around 3% w/w, at 150 bar around 7% w/w and at 60 bar around 14% w/w. Looking at the modifications in $scCO_2$/1,4-dioxane at 180 °C and 300, 150 and 60 bar (Fig. 3, respectively –▲–, – × – and –□–), all modifications resulted, within the experimental error (± 2 mmol/kg), in approximately the same carboxylic acid end group concentration after 24 h. Now we have to realise that upon

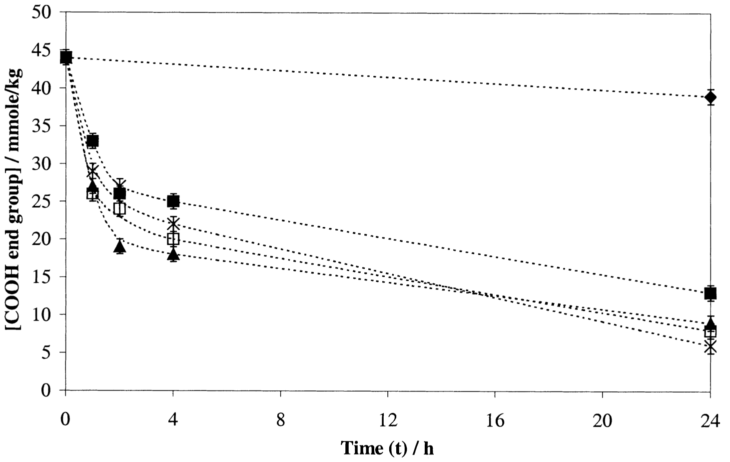

Fig. 3. Carboxylic acid end group concentration of PBT granules modified with 1,2-epoxybutane in time. Reaction conditions are: –◆–: $scCO_2$ at 120 °C and 300 bar; –■–: $scCO_2$ at 180 °C and 300 bar; –▲–: $scCO_2$ with 10 mol% 1,4-dioxane at 180 °C and 300 bar; – × –: $scCO_2$ with 10 mol% 1,4-dioxane at 180 °C and 150 bar; –□–: subcritical CO_2 with 10 mol% 1,4-dioxane at 180 °C and 60 bar. Error bars are ± 2.

Table 2
Carboxylic acid end group concentrations and relative viscosities of unmodified and 1,2-epoxybutane modified PBT granules and PBT powder, obtained after dissolving in HFIP and precipitating in MTBE

Entry	Material/modification conditions	[COOH end groups] of granules (±2 mmol/kg)	[COOH end groups] of powder (±2 mmol/kg)	η_{rel} of granules (±0.02)	η_{rel} of powder (±0.02)
1	Unmodified PBT	44	44	1.84	1.82
2	PBT modified in $scCO_2$, 120 °C, 300 bar, 24 h	39	40	1.83	1.85
3	PBT modified in $scCO_2$, 180 °C, 300 bar, 24 h	14	13	1.72	1.71
4	PBT modified in $scCO_2$/1,4-dioxane, 180 °C, 300 bar, 24 h	9	8	1.75	1.76
5	PBT modified in $scCO_2$/1,4-dioxane, 180 °C, 150 bar, 24 h	6	3	1.74	1.74

changing the pressure and keeping the 10-fold excess of 1,2-epoxybutane with respect to the carboxylic acid end groups of PBT the same, two parameters are changed, which are both capable of affecting the kinetics of the end group modification: the overall system pressure and the mentioned 1,2-epoxybutane concentration in the reaction medium. First of all, it was expected that the modification at 300 bar would result in the best blocking of the end groups, because the general observation is that a higher density of the medium results in a better swelling and sorption of the polymer [18,19]. However, based on the swelling of PET reported in Ref. [9], the swelling of highly crystalline PBT is estimated at only a few percent. Therefore, the effect of the degree of swelling upon end group modification is expected to be small. On the other hand, at higher system pressures, the modifier is likely to be transported into the PBT granules at a higher rate. Furthermore, with increasing pressure and density, the dielectric constant of the medium will increase, which results in a better interaction of the medium with the polymer and therewith in higher transportation rates of the modifier into the PBT granules. Coming back to the mentioned 1,2-epoxybutane concentration effect, a better end group modification is expected for the higher concentration of 1,2-epoxybutane in CO_2/1,4-dioxane. So we have two competing effects: a higher system pressure is competing with a lower modifier concentration. If the system is given sufficient time (e.g. 24 h), then the end group concentrations are almost the same. For long exposure times (24 h) a higher system pressure seems to compensate for a lower 1,2-epoxybutane concentration, resulting in a similar carboxylic acid end group concentration. For shorter modification times (2–4 h), when the system seems to be still far from equilibrium, the observed differences after modification at 60, 150 and 300 bar somewhat exceed the experimental error. However, whereas in view of the lowest modifier concentration the less complete blocking of the carboxylic acid end groups would be expected at 300 bar (Fig. 3, –▲–), the contrary is observed. Obviously, the lower concentration of the blocking agent at higher pressures is over-compensated by the higher pressure, forcing the modifier to enter the PBT granules at a higher rate.

In summary, the effects of swelling of the PBT granules and the concentration of 1,2-epoxybutane in CO_2/1,4-dioxane on the end group modification are both not as pronounced as expected, and therefore the modifications at 60, 150 and 300 bar and 180 °C resulted in quite similar end group concentrations. Moreover, for the PBT/CO_2/1,4-dioxane system the benefits of applying supercritical conditions over using subcritical conditions seem to be limited.

3.3. Determination of the relative and intrinsic viscosity of PBT

Modification of the carboxylic acid end groups of PBT in supercritical fluids was performed to obtain a polymer with increased hydrolytic stability. Three modified PBT samples, which showed a carboxylic acid end group concentration of around 10 mmol/kg after 24 h of modification, are interesting for hydrolytic stability tests, since this concentration of acid end groups is expected to be low enough to retard hydrolysis of the ester functionalities in the polymer chain in a sufficient way. The investigated samples are unmodified PBT, and PBT modified for 24 h in (1) $scCO_2$ at 180 °C and 300 bar, (2) $scCO_2$ with 10 mol% 1,4-dioxane at 180 °C and 300 bar and (3) $scCO_2$ with 10 mol% 1,4-dioxane at 180 °C and 150 bar. The carboxylic acid end group concentrations of these modified PBT granules before hydrolysis are respectively 14, 9 and 6 mmol/kg (see Table 2). Granules of all investigated PBT samples were placed in H_2O of 90 °C for a certain time. Hydrolysis should influence both mechanical and molecular properties of the polymer. When the polymer chain is hydrolysed, the solution viscosity of the polymer will decrease. Therefore, we considered the variation of the relative and intrinsic viscosity ($\eta_{rel} = \eta/\eta_0$ and $[\eta]$, respectively) with hydrolysis time as a measure for the hydrolytic stability of the PBT.

The intrinsic viscosity was determined using the following equation: $[\eta] = \eta_{inh} + (1/3)(\eta_{red} - \eta_{inh})$ [20].

In Fig. 4, the normalised intrinsic viscosity of hydrolysed PBT granules is given as a function of hydrolysis time. Since all four PBT samples did not have the same initial viscosity (see Table 2), the intrinsic viscosities were normalised, i.e. the calculated intrinsic viscosity at hydrolysis time *t* was divided by the intrinsic viscosity of the same

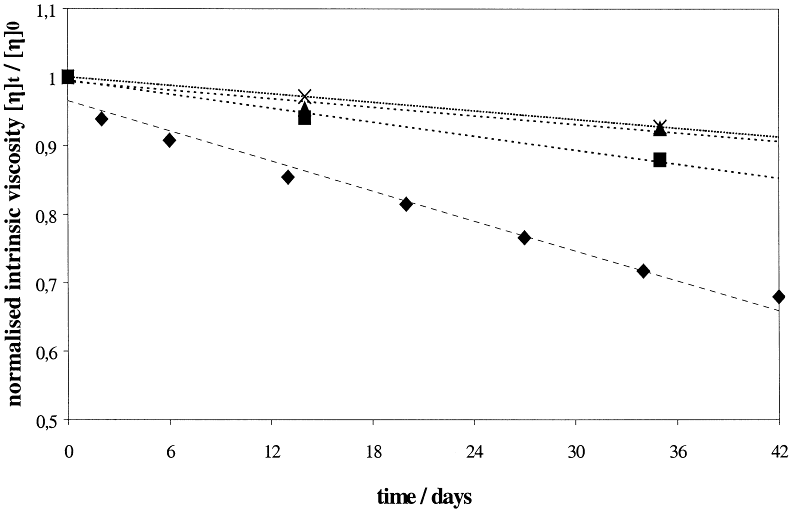

Fig. 4. Normalised intrinsic viscosity of PBT granules hydrolysed in time. –◆–: unmodified PBT; –■–: PBT, modified in $scCO_2$ at 180 °C and 300 bar for 24 h; –▲–: PBT, modified in $scCO_2$ with 10 mol% 1,4-dioxane at 180 °C and 300 bar for 24 h; – × –: PBT, modified in $scCO_2$ with 10 mol% 1,4-dioxane at 180 °C and 150 bar for 24 h.

sample at hydrolysis time $t = 0$. This resulted in a clear picture of the effect of end group concentration on the hydrolytic stability of the PBT. From Fig. 4, it is clear that the intrinsic viscosity of unmodified PBT (–◆–) decreases significantly faster in time that the $[\eta]$ of the end capped PBT samples. Clearly, modifying the carboxylic acid end groups in supercritical fluids has a positive effect on the hydrolytic stability. In Section 3.5, the crystallinity of the modified samples is discussed. The samples modified in $scCO_2$ showed increased crystallinities compared to the unmodified PBT. We are aware that with increasing crystallinity of PBT, the chemical resistance will increase as well, resulting in an improved stability. However, an increased crystallinity, results in a higher concentration of the carboxylic acid end groups in the amorphous phase as well, which subsequently results in an acceleration of the hydrolysis process. These two effects might just compensate each other, and we believe that the supercritical modification of the carboxylic acid end groups is the dominant factor for improving the hydrolytic stability.

PBT granules modified in CO_2/1,4-dioxane at 180 °C and 300 or 150 bar exhibit the best hydrolytic stability. Obviously the influence of pressure, applied during modification, on the extent of the carboxylic acid modification and on the hydrolytic stability of the PBT is negligible.

3.4. Size exclusion chromatography (SEC)

The hydrolysis experiments described in the previous section showed that the modification of the carboxylic acid end groups of PBT in supercritical fluids results in an enhanced hydrolytic stability compared to the unmodified PBT. The sensitivity of the intrinsic viscosity towards hydrolysis conditions is a measure for the hydrolytic stability. Hydrolysis of the ester functionalities in the polymer chain is also reflected in the molecular weights of the polymer. Therefore, the number and weight average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) as well as the weight distributions of the three modified PBT samples and the unmodified PBT, before and after hydrolysis, were determined. The values given in Table 3 are based on the exactly known molecular weights of the unmodified PBT. For unmodified PBT the $\bar{M}_n$ and $\bar{M}_w$ are respectively 16,200 and 34,000 g/mol ($\bar{M}_n$ accurately calculated, based on the end groups; $\bar{M}_w/\bar{M}_n$ value for the unmodified PBT was determined by SEC/DV at DSM Research, The Netherlands). Using the calibration based on PS standards (see Section 2) the obtained $\bar{M}_n$ value of unmodified PBT proved to be a factor 2.8 higher than the value which was accurately determined from the total number of end groups. Therefore, all number average molecular weights obtained by SEC were divided by a factor 2.8. Subsequently, $\bar{M}_w$s were calculated using the polydispersity indices ($\bar{M}_w/\bar{M}_n$), experimentally determined by SEC. Since for all samples the same procedure was used, the values for the molecular weights can be compared.

From Table 3 and Fig. 5 it can be seen that the modifications with 1,2-epoxybutane reduced $\bar{M}_w$ from 35,500 to about 30,000 g/mol. This is an indication that some hydrolysis of the polymer chains had occurred during the modifications in $scCO_2$. Although the PBT samples were dried before the modifications, traces of water can be hardly avoided. These traces can react with CO_2 with the formation of the slightly acidic H_2CO_3 (pK_a value of 6.4 in aqueous solution), which catalyses the hydrolysis of the ester bonds in PBT. Decreased relative viscosities were observed after modification (see Table 2), which could be either the result of (a) a different interaction of the polymer with the solvent during the viscosity measurements, or (b) a decrease in molecular weight. Here we have proven that degradation

Table 3
Number and weight average molecular weights and weight distributions of unmodified and modified PBT samples, before and after 5 weeks of hydrolysis

Entry	Materials/conditions of modification	$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	Unmodified PBT granules, before hydrolysis	34,000	16,200	2.1
2	Sample 1 after hydrolysis[a]	17,900	8,400	2.1
3	Unmodified PBT granules, after 24 h at 180 °C, before hydrolysis[b]	35,500	17,200	2.1
4	Sample 3 after hydrolysis	21,400	10,200	2.1
5	PBT modified in $scCO_2$, 180 °C, 300 bar, 24 h, before hydrolysis	29,500	15,100	1.9
6	Sample 5 after hydrolysis	25,000	12,500	2.0
7	PBT modified in $scCO_2$/10 mol% 1,4-dioxane, 180 °C, 300 bar, 24 h, before hydrolysis	30,700	15,400	2.0
8	Sample 7 after hydrolysis	25,700	12,700	2.0
9	PBT modified in $scCO_2$/10 mol% 1,4-dioxane, 180 °C, 15bar, 24 h, before hydrolysis	30,100	15,700	1.9
10	Sample 9 after hydrolysis	32,100	15,700	2.0

[a] Hydrolysed for 10 weeks instead of 5 weeks.
[b] Treatment in an oven in an argon atmosphere.

of the polymer had occurred. However, it is highly likely that the decrease in relative viscosity can be ascribed to both degradation and to a changed interaction with the solvent of the blocked end groups with the solvent.

In Fig. 6 the effect of thermal treatment and hydrolysis on the molecular weight distribution of the unmodified PBT samples is shown. From Fig. 6 and entries 1 and 3 in Table 3 it can be seen that the effect of the thermal treatment during 24 h at 180 °C is negligible. Increased $\bar{M}_n$ and $\bar{M}_w$ values, from 16,200 to 17,200 g/mol and from 34,000 to 35,500 g/mol, respectively, were observed. This clearly must be a result of post condensation.

The hydrolysis of the unmodified PBT sample without previous thermal treatment (Fig. 6 and entry 2, Table 3) results in a significant decrease in molecular weight. After 10 weeks in water of 90 °C, the $\bar{M}_n$ decreases from 16,200 to 8,400 g/mol and the $\bar{M}_w$ decreases from 34,000 to 17,900 g/mol. The hydrolysis of the unmodified PBT sample with previous thermal treatment (entry 4, Table 3) also results in a significant decrease in molecular weight. After 5 weeks in water of 90 °C, the $\bar{M}_n$ decreases from 17,200 to 10,200 g/mol and the $\bar{M}_w$ decreases from 35,500 to 21,400 g/mol.

The hydrolysis of the 1,2-epoxybutane modified PBT samples results in a much less pronounced decrease of the molecular weights. Fig. 7 and entries 3–10 in Table 3 show that the decrease in $\bar{M}_w$ is 40% for unmodified PBT and only around 16% for PBT samples, end capped with 1,2-epoxybutane. Clearly, the modification of the carboxylic acid end groups results in a hydrolytically more stable polymer.

3.5. Differential scanning calorimetry (DSC)

It is known that the crystallinity of several polymers can be induced or enhanced by $scCO_2$ [21–27]. Brantley et al. [21] used in situ FTIR spectroscopy to measure the sorption rate of CO_2 by poly(ethylene terephthalate) and to determine the initial crystallinity and the crystallinity after the exposure of PET to CO_2. Upon raising the temperature above the T_g (but below T_m) of a semi crystalline polymer,

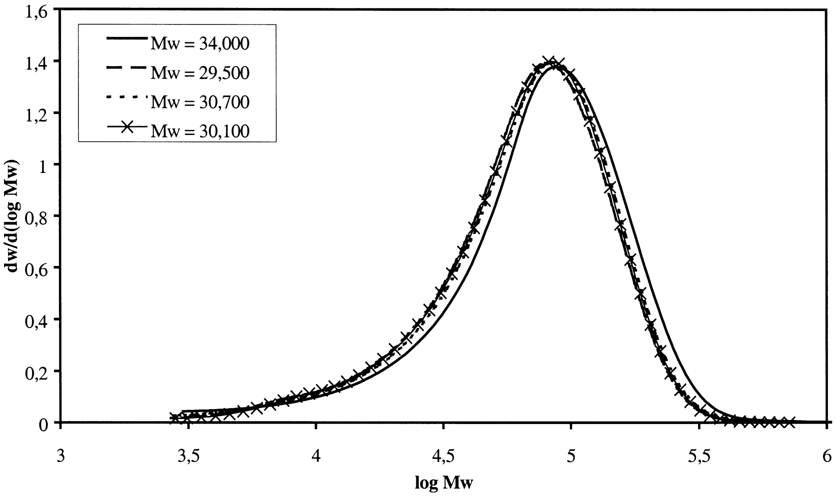

Fig. 5. Size exclusion chromatogram of PBT, starting material (—); PBT, modified in $scCO_2$ at 180 °C and 300 bar for 24 h (– – –); PBT, modified in $scCO_2$/10 mol% 1,4-dioxane at 180 °C and 300 bar for 24 h (- - -); PBT, modified in $scCO_2$/10 mol% 1,4-dioxane at 180 °C and 150 bar for 24 h (– × –).

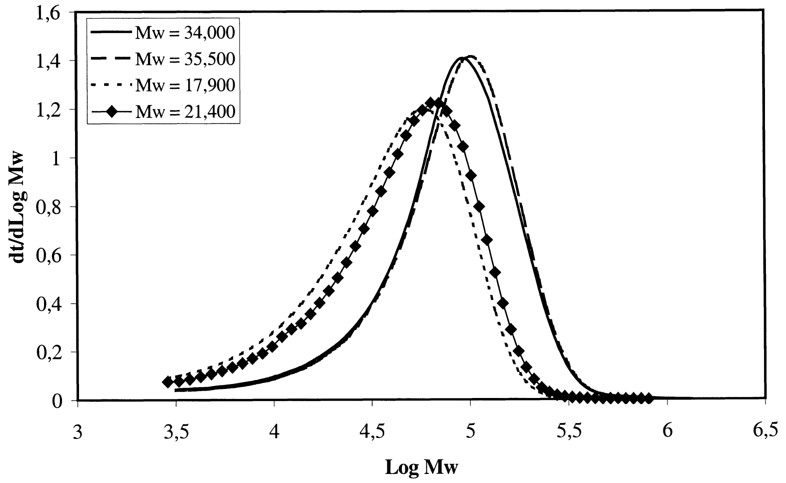

Fig. 6. Size exclusion chromatogram of unmodified PBT (—); unmodified PBT, after 24 h at 180 °C (– – –); unmodified PBT, after 10 weeks of hydrolysis (- - -); unmodified PBT, after 24 h at 180 °C followed by 5 weeks of hydrolysis (–◆–).

the mobility of the chains in the amorphous phase increases to such an extent that the chains can rearrange into the crystalline phase. This induced crystallinity can also be achieved by reducing the T_g to below the operating temperature by absorbance of plasticising CO_2.

After modification in $scCO_2$ some of the PBT granules appeared more brittle than unmodified PBT granules. To investigate whether or not the brittleness is caused by an enhanced crystallinity, DSC was used to determine the degree of crystallinity before and after the $scCO_2$ treatment. As was said earlier, a polymer with a higher crystallinity is less able to swell by sorption of a supercritical fluid. Less swelling and sorption results in a decreased transportation of the blocking agent into the polymer, and therewith results in a decreased modification rate. A higher degree of crystallinity, which might be generated during the modification process, could then explain the slower modification of the carboxylic acid end groups between around 4 and 24 h reaction time with respect to the initial stages, where the crystallinity raise is probably still limited. Furthermore, reduction of the free volume in the amorphous phase of the polymer upon end capping of the carboxylic acid end groups with 1,2-epoxybutane will result in a slower diffusion.

The crystallinity of the PBT, used as the starting material in this work, is around 37%. This value is based on a theoretical PBT with 100% crystallinity, with a known heat of fusion (ΔH_{fus}) of 140 J/g (Table 4, entry 1, data obtained from DSM Research, The Netherlands). As a result of the way of processing of the PBT granules, a higher degree of crystallinity was found for the core of the granules compared to the (frozen in) surface of the granules. It might therefore be that the CO_2 (and blocking agent) is predominately absorbed in the amorphous phase of the outer layer of the granules. To check whether a temperature of 180 °C, without the addition of CO_2, causes a higher degree of crystallinity, the unmodified PBT granules were placed in

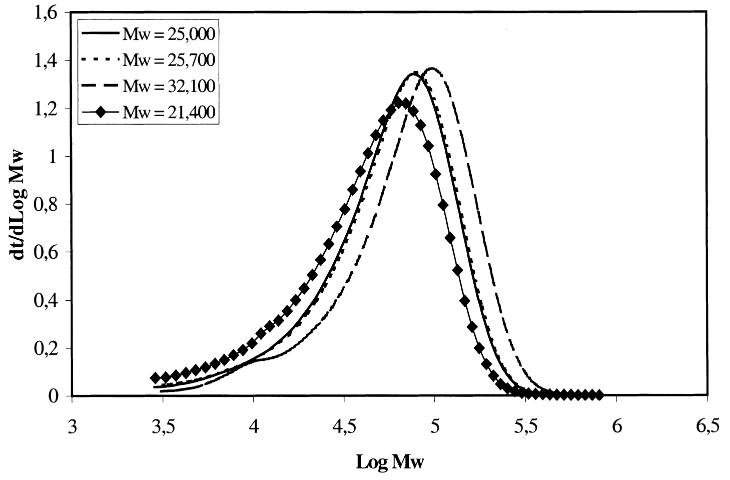

Fig. 7. Size exclusion chromatogram of PBT, modified in $scCO_2$ at 180 °C and 300 bar for 24 h followed by 5 weeks of hydrolysis (—); PBT, modified in $scCO_2$/10 mol% 1,4-dioxane at 180 °C and 300 bar for 24 h, followed by 5 weeks of hydrolysis (- - -); PBT, modified in $scCO_2$/10 mol% 1,4-dioxane at 180 °C and 150 bar for 24 h followed by 5 weeks of hydrolysis (– – –); unmodified PBT, after 24 h at 180 °C followed by 5 weeks of hydrolysis (–◆–).

Table 4
Estimated heats of fusion (ΔH_{fus}), degrees of crystallinity, peak melting temperature ($T_{m,peak}$), and peak crystallisation temperature ($T_{c,peak}$) for modified and unmodified PBT

Entry	Conditions of modification	$T_{m,1}$ (°C)	$\Delta H_{fus,1}$ (J/g)	Degree of cryst.$_1$ (%)	$T_{m,2}$ (°C)	$\Delta H_{fus,2}$ (J/g)	Degree of cryst.$_2$ (%)	T_c (°C)
1	Reference PBT (theoretical sample)	245	140	100	[a]	140	100	[a]
2	PBT (starting material)	226	53	37	226	51	36	175
3	PBT (starting material), after 24 h annealing at 180 °C	226	52	37	226	–	–	[a]
4	ScCO$_2$, 180 °C, 300 bar, 24 h	225	62	44	225	52	37	[a]
5	ScCO$_2$/10 mol% 1,4-dioxane, 180 °C, 300 bar, 24 h	228	76	54	225	52	37	[a]
6	ScCO$_2$/10 mol% 1,4-dioxane, 180 °C, 150 bar, 24 h	224	73	52	225	51	36	182

[a] Not determined.

an oven in an argon atmosphere and were annealed at 180 °C for 24 h. From this sample and the PBT starting material a thin slice from the middle of a granule (cross-section) was cut off and used for the DSC measurements (see Fig. 1). From three modified samples (Table 4, entries 4–6), the granules were ground and the powder was used for DSC measurements. In Table 4, the estimated heats of fusion, obtained from DSC measurements, are given.

When comparing the crystallinity of the unmodified PBT after 24 h annealing at 180 °C (entry 3) with the degree of crystallinity of the starting material (entry 2), no change is observed. It can be therefore concluded that merely annealing the PBT granules does not affect the degree of crystallinity. When comparing the crystallinities of the modified PBT samples (CO$_2$, 180 °C, entries 4–6, Table 4) with the crystallinity of unmodified PBT after 24 h annealing at 180 °C (entry 3), it is obvious that all three modified PBT samples have increased crystallinity compared to the unmodified PBT. The PBT modified in CO$_2$/10 mol% 1,4-dioxane shows a more pronounced increase in crystallinity, compared to PBT modified in pure CO$_2$. This clearly indicates that pure CO$_2$ enhances the degree of crystallinity, and that a mixture of CO$_2$ with 10 mol% 1,4-dioxane even further enhances the degree of crystallinity. This increase can be ascribed to the plasticising effect caused by impregnation of CO$_2$ and CO$_2$/1,4-dioxane, and not by an annealing phenomenon at 180 °C.

Normally an initial high degree of crystallinity of the polymer would result in a worse end group modification. However, the crystallinity is only gradually increasing during the modification caused by impregnation of the supercritical fluid, which at the same time is the carrier of the blocking agent. Obviously, the gradually increasing crystallinity does not have a very pronounced influence on the modification of the end groups.

Disadvantages of the higher degree of crystallinity are that more energy is needed to melt the granules and more dust will form during transportation of the granules before melt processing. To check whether the end group modification has a nucleating effect on the crystallisation the modified samples were molten and recrystallised (results also in Table 4). The degrees of crystallinity of the modified and unmodified samples have regained their original values after melting and subsequent crystallisation ($\Delta H_{fus,2} = 51$ J/g for both modified and unmodified PBT). The crystallisation temperature (T_c) of modified PBT ($T_c = 182$ °C, entry 6) is significantly higher than the crystallisation temperature of unmodified PBT ($T_c = 175$ °C, entry 2). The higher value for the T_c can be a result of 1) a nucleating effect (caused by the new end groups) or 2) a decrease in molecular weight. A nucleating effect seems to be unlikely, since the modified end groups look similar to the unmodified end groups (respectively, secondary and primary alcohols, see Fig. 2). The higher T_c is probably caused by the observed decrease in molecular weight ($\bar{M}_w$ decreases from 34,000 to 30,100 g/mol; see Table 3). So, no indications are obtained that the PBT crystallisation is accelerated by a nucleating effect, but the crystallisation is not hindered either.

4. Conclusions

In this paper we have shown that it is possible to block carboxylic acid end groups of PBT with 1,2-epoxybutane in supercritical and subcritical fluids. From model reactions with PBT in organic liquids, it was found that the use of 1,4-dioxane as a modifier for the supercritical medium resulted in improved blocking of the carboxylic acid end groups, which is ascribed to a higher degree of swelling. Best results were obtained for the modification in scCO$_2$ with 10 mol% 1,4-dioxane at 180 °C. A decrease of the carboxylic acid end group concentration from 44 mmol/kg to approximately 10 mmol/kg was achieved. This low concentration of acid end groups resulted in a significantly enhanced hydrolytic stability, which was demonstrated by measuring, both for unmodified and for 1,2-epoxybutane blocked PBT, the intrinsic viscosity as a function of hydrolysis time as well as the number and weight average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) before and after hydrolysis. After the modification, the PBT granules appeared more brittle than the unmodified PBT granules. DSC measurements showed an increased percentage of crystallinity for these modified samples, which was induced by the plasticising effect of CO$_2$/1,4-dioxane at 180 °C. No indications were obtained that the 1,2-epoxybutane modified end groups exhibit a nucleating effect on the PBT crystallisation. In spite of the mentioned disadvantages, related to an enhanced degree of crystallinity, we believe that the use of supercritical fluids in polymer modification has interesting opportunities.

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References

[1] Zimmermann H, Kim NT. Polym Engng Sci 1980;20:680.
[2] Sawada S, Kamiyama K, Ohgushi S, Yabuki K. J Appl Polym Sci 1991;42:1041–8.
[3] Buxbaum LH. Angew Chem, Int Ed Engl 1968;7:182–90.
[4] De Giorgi MR, Cadoni E, Maricca D, Piras A. Dyes Pigm 2000;45: 75–9.
[5] Veugelers WJTh, Gooijer H, Gerritsen JW, Woerlee GF. Eur. Pat. Appl. Patent no. 1126072; 2001. 7 p
[6] Bach E, Cleve E, Schollmeyer E. Process Technol Proc 1996;12: 568–81.
[7] Poliakoff M, George MW, Howdle SM, Bagratashvili VN, Han BX, Yan HK. Chin J Chem 1999;17(3):212–22.
[8] Buback M, Rindfleish F. Chem Ing Tech 1995;67:591–4. Buback M, Elstner U, Rindfleish F, McHugh MA. Macromol Chem Phys 1997; 198:1189–96.
[9] Von Schnitzler J, Eggers R. J Supercrit Fluids 1999;16:81–92.
[10] Muth O, Hirth Th, Vogel H. J Supercrit Fluids 2000;17:65–72.
[11] McHugh MA, Krukonis VJ. Supercritical fluid extraction: principles and practice. London: Butterworth; 1986.
[12] Reid RC, Prausnitz JM, Poling BE. The properties of gases and liquids. London: Mc Graw-Hill; 1987.
[13] Kay WB. Ind Engng Chem 1936;28:1014–9.
[14] Sun YJ, Hu GH, Lambla M, Kotlar HK. Polymer 1996;37(18): 4119–27.
[15] L. Leemans, personal communication, DSM Research, Geleen, The Netherlands
[16] T. Loontjens, personal communication, DSM Research, Geleen, The Netherlands
[17] Porter SR, Taylor LT. J Chromatogr A 1999;855:715–21.
[18] Ellmann J. PhD Thesis. Polymerization and reactive coating in supercritical CO_2, University of Ulm, Germany; 2001
[19] Wissinger RG, Paulaitis ME. J Polym Sci, Part B: Polym Phys 1987; 25:2497–510.
[20] Rudin A. The elements of polymer science and engineering. San Diego, CA: Academic Press; 1999.
[21] Brantley NH, Kazarian SG, Eckert CA. J Appl Polym Sci 2000;77: 764–75.
[22] Lambert SM, Paulaitis ME. J Supercrit Fluids 1991;4:15–23.
[23] Beckman E, Porter RS. J Polym Sci, Part B: Polym Phys 1987;25: 1511–7.
[24] Zhong Z, Zheng S, Mi Y. Polymer 1999;40:3829–34.
[25] Chiou JS, Barlow JW, Paul DR. J Appl Polym Sci 1985;30(9): 3911–24.
[26] Gross SM, Goodner MD, Roberts GW, Kiserow DJ, DeSimone JM., Book of Abstracts, 218th ACS National Meeting, New Orleans; 1999. p. 22–6
[27] Shieh YT, Su JH, Manivannan G, Lee PHC, Sawan SP, Spall WD. J Appl Polym Sci 1996;59:695–705.