

Characterization of Low Molecular Weight Carboxyl-Terminated Polyamides Obtained by Reactive Extrusion of Polyamide 6 with Trimellitic Anhydride

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SYNOPSIS

Reactive extrusion has been applied as a very effective and fast process for controlled chemical degradation of a commercial polyamide 6 with trimellitic anhydride in the melt. A reaction mechanism based mainly on the amide/anhydride reaction has been discussed and confirmed by measurements of the solution viscosity, end group analysis, SEC, NMR, and IR spectroscopy. The systematic loss of molecular weight of the polyamides resulting from PA chain rupture and the formation of imide linkages and carboxyl end groups were investigated. The theoretical values of molecular weight and end group concentration of the obtained oligoamides predicted by the reaction mechanism are in good agreement with the experimental ones. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It is known from Xanthos¹ that the controlled molecular weight degradation and introduction of functional groups into polymer backbone or at chain ends are important types of chemical reactions performed by reactive extrusion. If the chemical reaction in the polymer melt is fast enough (some minutes) a corotating intermeshing twin-screw extruder should be applied as chemical reactor because of the following advantages:^{2,3}

- continuous melt processing with narrow residence time distribution;
- flexibility due to modular design including various possibilities for material addition, devolatilization, temperature and pressure control, residence time variation;
- enhanced mixing, reaction, and heat transfer;
- large ranges of pressure (0–500 atm), temperature (70–500°C), and melt viscosity (few mPa–100,000 Pa).

One of the characteristics of reactive melt processing is the opportunity of a modified reaction behavior of a polymer as a result of the extreme conditions in the extruder (intensive mixing, shearing) in difference to its well-known reaction parameters in laboratory scale. It is therefore important and necessary also from the technological and quality point of view to characterize the mechanism and products of reactive extrusion processes carefully.

On-line methods are very desirable, which allow a continuous extrusion monitoring and can be extended to process control systems later. Recently we have reported our first experiments to monitor the melt reaction of styrene–maleic anhydride copolymers with aliphatic amines in a twin-screw extruder using infrared spectroscopic in- and on-line methods.^{4,5}

Different technologies of recycling and down-cycling have been applied to utilize polymer waste.⁶ One way to use grading polyamide 6 waste in a very effective and fast process without any solvents could be the selective chemical degradation of the polymer in its molten state applying the twin-screw extruder. As reported in our previous works,^{7,8} the long polymeric chains can be ruptured very fast during reactive extrusion in a defined matter, if a suitable low molecular weight rupture substance was added. By the controlled degradation of the high molecular

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weight starting PA6, functionalized amide polymers and oligomers were produced, which can be purified by the classical methods of chemical engineering. These products should be applicable to synthesize new block copolyamides. Taeger et al.⁶ described the formation of copolyamides using such amino- and carboxyl-terminated amide oligomers resulting from the PA6 degradation in the melt.

In a recent work by Marechal et al.⁹ PA6 was blended in a batch mixer at 240°C up to 50 min with phthalic or *n*-octadecyl succinic anhydride to study the nature of the polyamide/anhydride reaction in the melt. For the chemical degradation of PA12, Hartkopf, auf der Heyde, and Meyer¹⁰ used adipic acid. The melt reaction was carried out in laboratory scale at 220–250°C for 4 h. From their ¹³C-NMR spectroscopic results they concluded that after the reaction the acid groups were on the chain ends of the formed oligomers or inserted into the chain to a lesser degree.

In our study we characterize the products of the reactive melt processing of a commercial polyamide 6 with trimellitic anhydride in an extruder mainly by viscosimetry, SEC, end group analyses, and spectroscopy. The aim was to confirm that the described degradation process of PA6 under extruder conditions needs less than five minutes and proceeds according to the proposed mechanism. The molecular weight and the new functional groups were discussed particularly.

EXPERIMENTAL

Materials

The polyamide 6 (PA6) used for degradation experiments was a Miramid ($\bar{M}_n^0 = 22,600$ g/mol) of the Leuna-Werke AG (Germany); the concentration of amino end groups was about 70 mEq/kg and of carboxyl end groups about 50 mEq/kg. The granules melt at 227°C (DSC). Trimellitic anhydride (TMAAn) from Amoco Chem. (USA) is a white powder with $M(\text{TMAAn}) = 192$ g/mol and a melting point of 168°C. Both materials were dried at 80°C for at least 10 h in a vacuum oven to remove sorbed water before processing.

Preparation of the Terminated Amide Oligomers

Laboratory Preparation (Experiments of the Series I and V)

An amount of m_0 g PA6 was mixed with m_d g TMAAn and melted in a 3-necked flask (*L*) or steel vessel

(*V*) under stirring and nitrogen purging. The degradation reaction was carried out in the melt for 15–20 min at 275°C.

Reactive Extrusion Process (Experiments of the Series E and ER)

PA6 and TMAAn were mixed in the calculated weight ratios m_0/m_d in different ways: Prior to extrusion TMAAn was placed on the surface of the PA granules using a concentrated acetone solution. Then the solvent was eliminated in a vacuum oven at 30°C for 2 h (*E*). TMAAn was also mixed in the powder form with PA6 prior extrusion or added to the molten PA6 into the extruder (*ER*). Twin-screw extruders ZDS-K 28 and ZSK 30 (Werner & Pfleiderer) were used. The temperatures of the barrel and the die were in the range of 250 to 275°C. At a screw speed of 30 r.p.m. (ZDS-K 28, experiments *E*) the reaction time during melt mixing was approximately 2 min, and at 80 r.p.m. (ZSK 30, experiments *ER*) 3 min, respectively. The extruded products having very low melt viscosity were quenched in a water bath, pelletized, and dried.

Methods

Solution Viscosity

The solution viscosity was measured with an Ubbelohde viscosimeter at 100°C using a mixture of *o*-dichlorobenzene/*o*-cresol 1/1 (v/v). The polymer concentration was $c = 0.2$ g/dL. From the relative viscosities η_{rel} the reduced viscosities η_{red} were calculated according to $\eta_{\text{red}} = (\eta_{\text{rel}} - 1)c^{-1}$.

Extraction Procedure

Prior to characterization all samples were extracted in water and tetrahydrofuran. The water-soluble content was determined gravimetrically on samples which were refluxed for 5 h in boiling water (500 mg/30 ml water), hot filtrated, and dried.

Size-Exclusion Chromatography (SEC)

High-temperature SEC equipment (KNAUER) included a Merck-Hibar RT 250-7 column (LiChrogel PS 400, 10 μm) and a DRI detector was used for molecular weight investigations. The eluent was a mixture of *o*-cresol/*o*-dichlorobenzene 1/1 (v/v) with a flow rate of 1 mL/min. Sample amounts of 0.2 mg were injected as 1% solution. The measurements were carried out at 100°C. Polystyrene (PS) with a narrow molecular weight distribution was used for calibration of the chromatographic system.

End Group Analysis

The concentration of carboxyl end groups [COOH] was determined by potentiometric titration using a 0.5 n KOH methanol solution. Amounts of 3 to 10 g of the degraded PA6 were dissolved in 50 to 100 ml of a *o*-cresol/chloroform mixture 6/4 (v/v) with small amounts of methanol for titration. Amino end groups [NH₂] were titrated using 0.02 n HCl *n*-propanol solution and a sample solution of 0.5 g polymer in 20 mL phenol/*n*-propanol 3/1 (v/v).

Thermal Analysis

Melting points were determined by DSC (DSC 7, Perkin-Elmer).

Spectroscopy

The NMR spectra were obtained using a Bruker AMX 300 spectrometer operating at 300.13 MHz for ¹H and at 75.475 MHz for ¹³C. Samples were dissolved in trifluoroacetic acid/chloroform-*d* 3/1 (v/v).

The IR spectra were collected on a Bruker IFS 66 FTIR spectrometer. Thin films of the polyamides were cast from their formic acid solution and transmission spectra were recorded with a spectral resolution of 2 cm⁻¹ coadding 32 scans/spectrum.

RESULTS AND DISCUSSION

Mechanism of the PA6/Trimellitic Anhydride Reaction

For the reaction of PA6 with anhydrides in the melt two different mechanisms are described in the literature.^{9,11} The first one is the reaction of the anhydride with the amino end groups of the PA6 and the second one is the amide/anhydride reaction that gives chain rupture. Both reactions modify the carboxyl and amino end group concentration and chain length or molecular weight, respectively. As explained by Lehmann et al.¹² in detail we favor the second mechanism as the dominant one to describe the reaction of the PA6 with trimellitic anhydride (TMA) during reactive extrusion.

In Scheme 1 all the reactions occurring in the melt are summarized:

The amino end groups react with TMA as a carboxyl group containing aromatic anhydride. Stable imide linkages and new carboxyl end groups were formed (a). Simultaneously, amide linkages in the PA chains were cut by the anhydride and further carboxyl end groups were formed after imidization (b). The reactivity of the carboxyl groups in the

polymer melt is very high.¹² Under the excellent mixing conditions in the twin-screw extruder acidolytic and amide–amide interchange reactions were accelerated. As a result, oligomers with more uniform chain length and narrower molecular weight distribution were produced (c). In this step the carboxyl end group concentration does not change.

Based on the proposed reaction mechanism a theoretical number-average molecular weight \bar{M}_n^{calc} and a theoretical carboxyl end group concentration [COOH]^{calc} of the produced carboxyl-terminated oligomers can be calculated as a function of the molecular weight \bar{M}_n^0 , the end group concentration [COOH]⁰ and the weight ratio m_0/m_d of the initial PA6 and TMA used in the degradation process.⁶

$$\bar{M}_n^{\text{calc}} = M(\text{TMA})m_0/m_d + \bar{M}_n^0m_d/m_0 \quad (1)$$

$$[\text{COOH}]^{\text{calc}} = [\text{COOH}]^0 2\bar{M}_n^0/\bar{M}_n^{\text{calc}} \quad (2)$$

For example, to produce an oligomer with $\bar{M}_n^{\text{calc}} = 14700$ g/mol from 3 kg PA6 with $\bar{M}_n^0 = 22,600$ g/mol we added 40 g TMA.

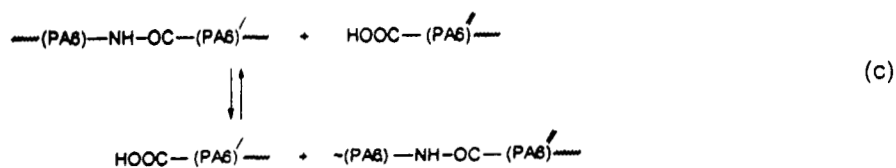
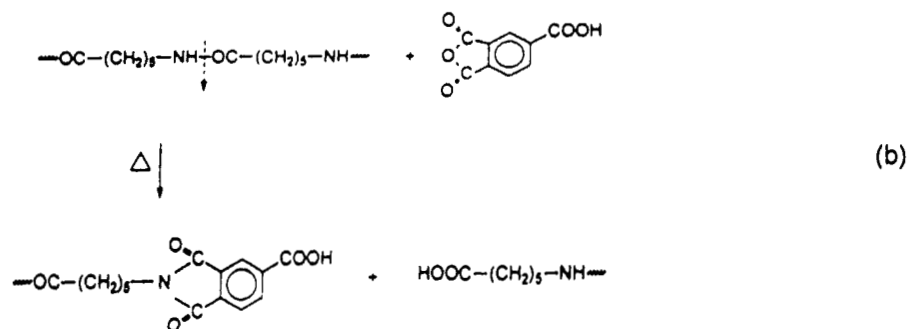
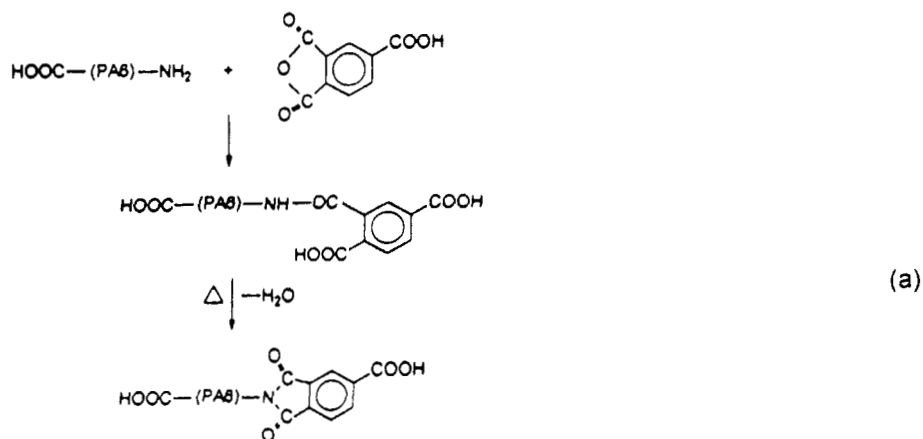
The following analytical results confirm the proposed mechanism.

Systematic Loss of Molecular Weight of the Polyamides Resulting from PA Chain Rupture

Figure 1 demonstrates the molecular degradation of the PA6 during reactive extrusion with TMA. At higher amounts of the rupture substance TMA (decreasing \bar{M}_n^{calc} values [eq. (1)]) the values of the reduced solution viscosity of the degraded PA samples decrease independently of the applied process technology (experiments L and RE). The viscosity loss is nearly linear. A $[\eta] - \bar{M}_n^{\text{calc}}$ correlation was obtained¹² using the η_{red} values and the approximation $\eta_{\text{red}} \sim [\eta]$ valid for the applied low concentration.

The water-soluble content (Fig. 2) is about 1–3% down to 5000 g/mol as well and increases at lower \bar{M}_n^{calc} . Oligoamides, caprolactam, and amino acids were found spectroscopically in the water extract. It can be concluded that controlled degradation and complete reaction proceed down to \bar{M}_n^{calc} values of about 5000 g/mol.

The melting points of the degraded PA samples change only slightly from 227 to 220°C in this \bar{M}_n range; the degradation is connected with a strong decrease of melt viscosity. In all experiments the concentration of the added anhydride is much higher than the original amino end group concentration of the polyamide. Therefore, a strong increase of car-



Scheme 1 Reaction mechanism of degradation and end group functionalization of polyamide 6 (PA6) with trimellitic anhydride (TMA). (a) Reactions of the amino end groups; (b) PA chain rupture; (c) acidolytic and amide–amide interchange reactions, (PA6), (PA6)', (PA6)" = polyamide chains of different length.

boxyl end group concentration is to be expected after proceeding with the reactions (a) and (b) as shown in Scheme 1, particularly since additional carboxyl groups are introduced with the TMA. After the fast consumption of the small amount of initial amino end groups [step (a) in Scheme 1] the most

TMA react with the amide bonds of the polyamide chains [step (b) in Scheme 1] leading to a decrease of molecular weight and to the formation of new carboxyl end groups. Note that the initial amino end group/chain amide group ratio in the used PA6 is about 1/200. Therefore, the amide/anhydride re-

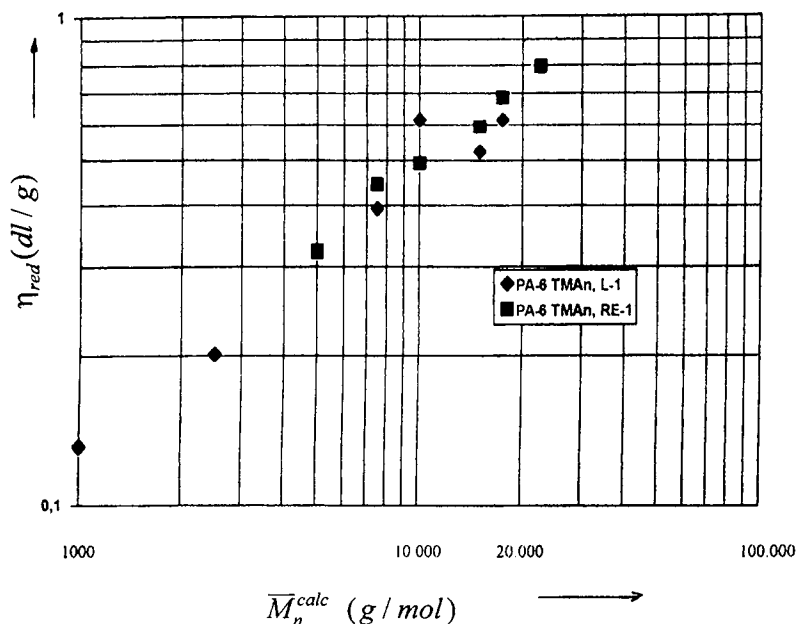


Figure 1 Solution viscosity η_{red} of degraded PA samples with different \bar{M}_n^{calc} , obtained by different processes. L-1 = laboratory preparation, RE-1 = reactive extrusion.

action (b) should play a more important role during the short reaction time in the extruder than the amine/anhydride reaction (a).

In Figure 3 the calculated values of the amino and carboxyl end group concentration based on the proposed reaction mechanism are compared with the

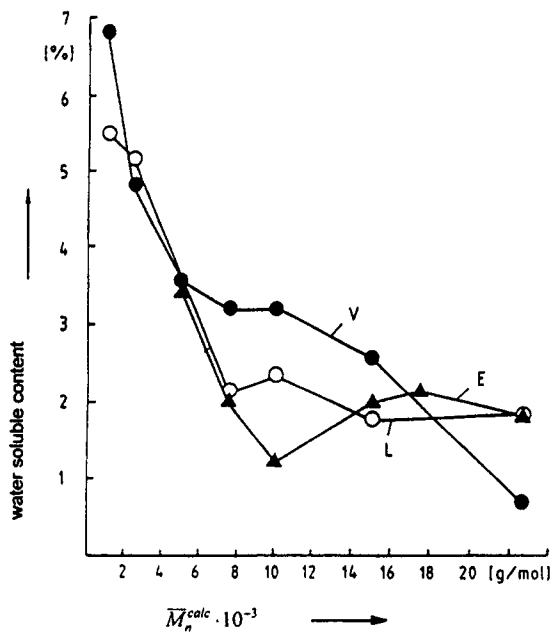


Figure 2 Water-soluble content of degraded PA samples with different \bar{M}_n^{calc} . L and V = laboratory preparation, E = reactive extrusion.

experimental values. The [COOH] values agree very well with regard to the titration error (about 10%).

After the degradation [NH₂] should reach values near zero. Nevertheless, we measured a low amino group concentration (Fig. 3). It is known from Marchal et al.⁹ that hydrolysis and condensation reactions proceed in the PA melt: According to their proposed mechanism 1 the anhydrides react with amine chain ends and consequently, the equilibrium of the polyamide is affected. Re-equilibrium will oc-

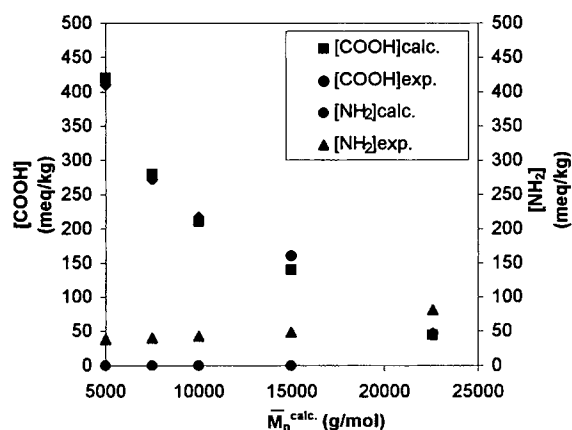


Figure 3 End group concentration of degraded PA samples with different \bar{M}_n^{calc} . [COOH]exp. and [NH₂]exp. = experimental values from titration, [COOH]calc. and [NH₂]calc. = calculated values based on the proposed mechanism.

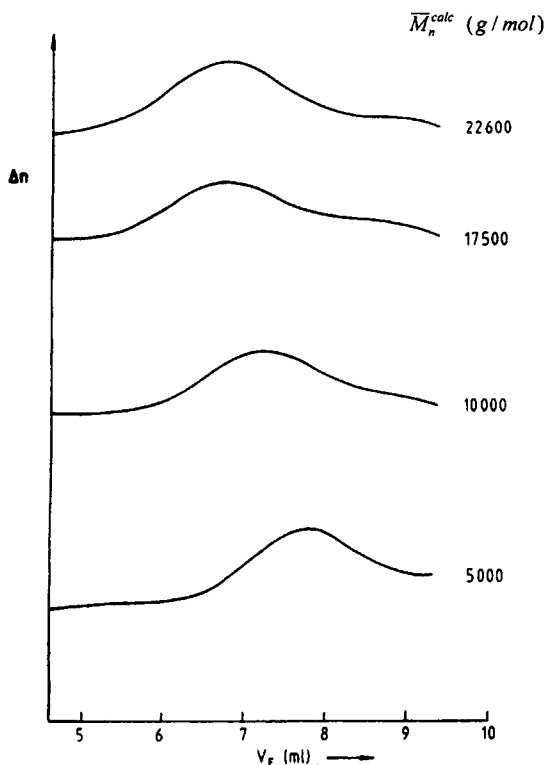


Figure 4 SEC curves of degraded PA samples with different \bar{M}_n^{calc} .

cur by hydrolysis consuming the formed water [see (a) in Scheme 1], with the formation of new amino and carboxyl end groups. Therefore it is obvious that the amino groups do not disappear completely. However, it should be pointed out that the melt was degassed continuously during our reactive extrusion to remove the water which is necessary for hydrolysis.

It is surprising that the discovered amino groups are not very active in solid state postcondensation experiments which could be performed at temperatures below the PA melting point. Usually such procedures were applied by polyamide manufacturers to increase the molecular weight. In our corresponding experiments¹² using degraded low molecular weight PA samples, no essential increase of molecular weight was obtained. With regard to these results and to the titration error we think that the amino end group concentration in our carboxyl-terminated samples is actually negligible in comparison with the concentration of the carboxyl end groups.

Figure 4 shows the SEC curves of the initial and degraded PA samples. As expected the degradation is connected with a continuous shifting of the SEC peaks to higher values of retention volume V_E that means lower molecular weights. There is no re-

markable change in line shape. The molecular weight and molecular weight distribution data obtained from the SEC are presented in Figure 5. From the systematic loss of \bar{M}_n and \bar{M}_w with decreasing \bar{M}_n^{calc} it can be concluded that the degradation is a controlled process forming products with normal molecular weight distribution ($\bar{M}_w/\bar{M}_n \sim 2$).

Identification of Terminal Carboxyl Groups and Imide Linkages

The formation of imide linkages and the functionalization of the polymer chain ends by carboxyl groups as a result of the PA6/TMAN reaction were demonstrated by ¹H-NMR, ¹³C-NMR, and IR spectroscopy.

The terminal carboxyl groups give the corresponding carbonyl signals [(7,10) in the NMR spectra Fig. 6(b)]. The trimellitic imide groups were identified by the following signals: aromatic carbon atoms [1–6 in Fig. 6(b)], aromatic hydrogen atoms [2, 5, 6 in Fig. 6(a)], imide carbonyl groups [8 in Fig. 6(b)]. Sometimes small additional signals of incorporated chain imide segments were found.

In the IR spectra (Fig. 7) of the degraded PA samples two new characteristic absorption bands appear, indicating the imide linkage. The 1773 cm^{-1} and 1717 cm^{-1} bands come mainly from the symmetric and antisymmetric carbonyl stretching mode of the cyclic aromatic imide groups. Particularly the 1717 cm^{-1} band is also caused by the CO stretching vibration of the carboxyl groups. The extinction coefficients of the aromatic CH and CC vibrations of the imide are somewhat lower, therefore these bands could not be observed in the spectra.

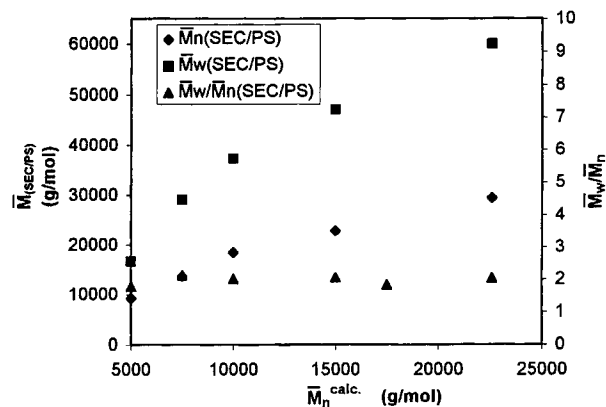


Figure 5 Molecular weights and molecular weight distribution \bar{M}_w/\bar{M}_n obtained from SEC data (SEC/PS = calibrated using polystyrene standards).

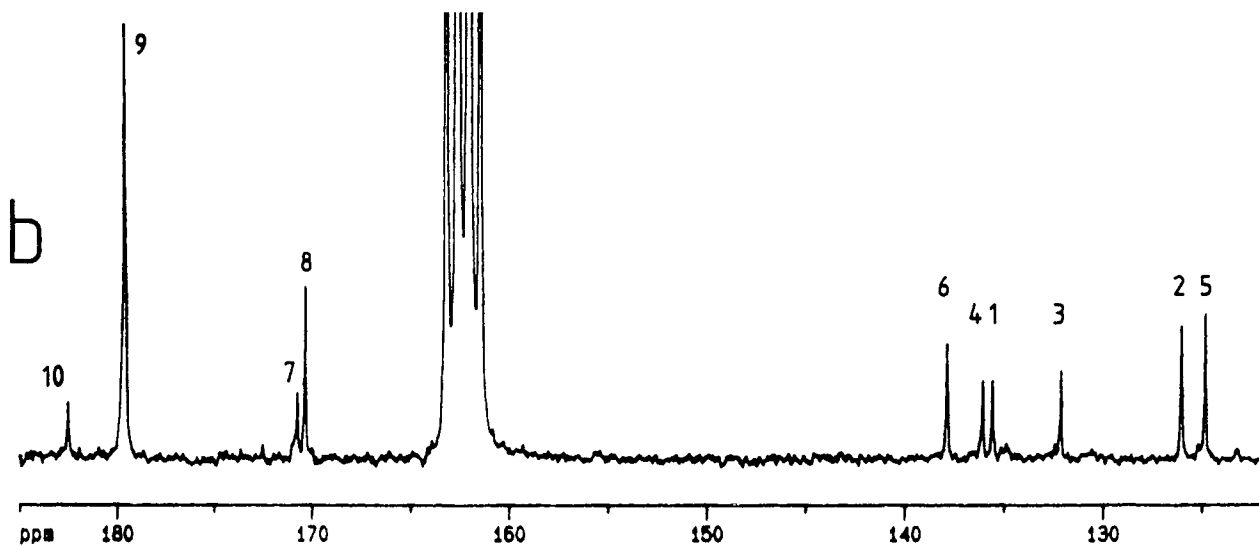
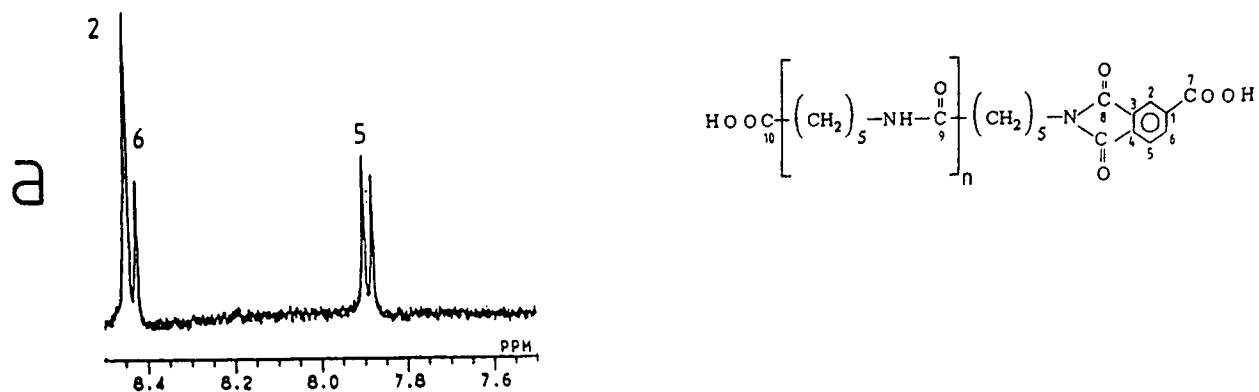


Figure 6 NMR spectra of a degraded PA sample, $\bar{M}_n^{\text{calc}} = 5000$ g/mol, product of reactive extrusion. (a) $^1\text{H-NMR}$, (b) $^{13}\text{C-NMR}$; for assignments of NMR peaks see peak numbers and chemical structure.

CONCLUSION

Reactive extrusion is an effective continuous process for a controlled chemical degradation of commercial polyamide 6 in the molten state without solvents. To rupture the long polyamide chains, anhydrides as low molecular weight organic substances are suitable. Using trimellitic anhydride carboxyl-termin-

nated oligoamides with desired molecular weights were obtained. We think that the amide/anhydride reaction is the dominant reaction in the melt during extrusion. The proposed reaction mechanism was supported by different analytical investigations. The results from viscosimetry, end group titration, and SEC confirm the controlled molecular degradation and the expected molecular weights of the degraded

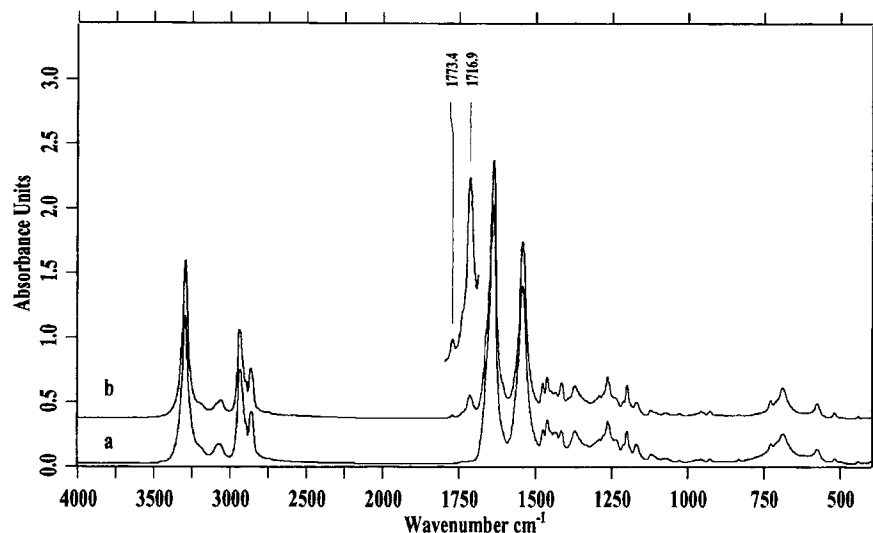


Figure 7 IR spectra of (a) initial PA6, $\bar{M}_n^0 = 22,600$ g/mol; (b) degraded PA sample, $\bar{M}_n^{\text{calc}} = 5000$ g/mol, product of reactive extrusion.

PA samples. The formed carboxyl end groups and imide linkages were identified by NMR and IR spectroscopy.

The application of the described oligoamides for the synthesis of copolyamides will be tested in further experiments.

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