

## Designing Oligomeric Ethylene Terephthalate Building Blocks by Chemical Recycling of Polyethylene Terephthalate

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**ABSTRACT:** The intelligent recycling of plastics waste is a major concern. Because of the widespread use of polyethylene terephthalate, considerable amounts of PET waste are generated that are ideally re-introduced into the material cycle by generating second generation products without loss of materials performance. Chemical recycling methods are often expensive and entail environmentally hazardous by-products. Established mechanical methods generally provide materials of reduced quality, leading to products of lower quality. These drawbacks can be avoided by the development of new recycling methods that provide materials of high quality in every step of the production cycle. In the present work, oligomeric ethylene terephthalate with defined degrees of polymerization and defined molecular weight is produced by melt-mixing PET with different quantities of adipic acid as an alternative pathway of recycling PET with respect to conventional methods, offering ecofriendly and economical aspects. Additionally, block-copolyesters of defined block length are designed from the oligomeric products. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39786.

**KEYWORDS:** polyesters; recycling; thermoplastics; degradation

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### INTRODUCTION

Polyethylene terephthalate (PET) is a semi-crystalline thermoplastic polyester prepared from terephthalic acid and ethylene glycol. Among many other applications, PET is widely used for manufacturing high-strength fibers, polymer films, and beverage bottles. The worldwide consumption of PET currently amounts to ca. 13 million tons, of which 9.5 million tons are processed in the textile industry, 2 million tons are used for the manufacture of audio and video tapes, and 1.5 million tons are consumed in the packaging industry.<sup>1,2</sup> Correspondingly, because of its widespread use, considerable amounts of PET waste are generated on a daily basis and the development of suitable recycling methods that allow re-integrating PET waste into the material cycle are of great technological interest.<sup>3–8</sup>

The recycling of plastic waste, including PET, can be done in various ways (Figure 1). A popular form of the recycling of used polymeric materials is the so-called "material recycling", which consists of collecting, crushing, and granulating the plastics waste, and re-introducing it into the production cycle. Recycled PET is mainly used for the manufacture of products that are not required to meet high quality standards.<sup>2</sup>

Although in favorable cases the recycling may extend over several polymer generations, structural deterioration is unavoidable

and leads to materials of lower quality than the original product (down-cycling). PET reutilization ultimately ends in the final disposal of the polymer. Major reasons for the down-cycling of polymers are their inhomogeneity, the presence of impurities and the accumulation of structural defects. In contrast to low molecular weight compounds, macromolecules are difficult or not at all to clean from structural defects or impurities that accumulate during processing and their product life time.<sup>12</sup> This is the case even with very homogeneous wastes. Down-cycling drastically limits the range of polymer waste that can be used for high-quality recycling products.

Down-cycling can be circumvented by complete depolymerization of the waste polymer to second-generation monomers, which are then re-used as polymerization raw materials (Figure 1). This approach is very common but has several disadvantages. Large amounts of often very toxic chemicals are required for the regeneration and purification of the monomers that entails financial and ecological issues.<sup>3,17–20</sup> Furthermore, chemical de-polymerization is often conducted under high temperature and high pressure conditions and, therefore, involves special equipment and high energy consumption.<sup>2,4</sup>

An interesting alternative for material recovery avoids complete de-polymerization by maintaining a defined molecular weight of the waste polymer and generating defined oligomeric

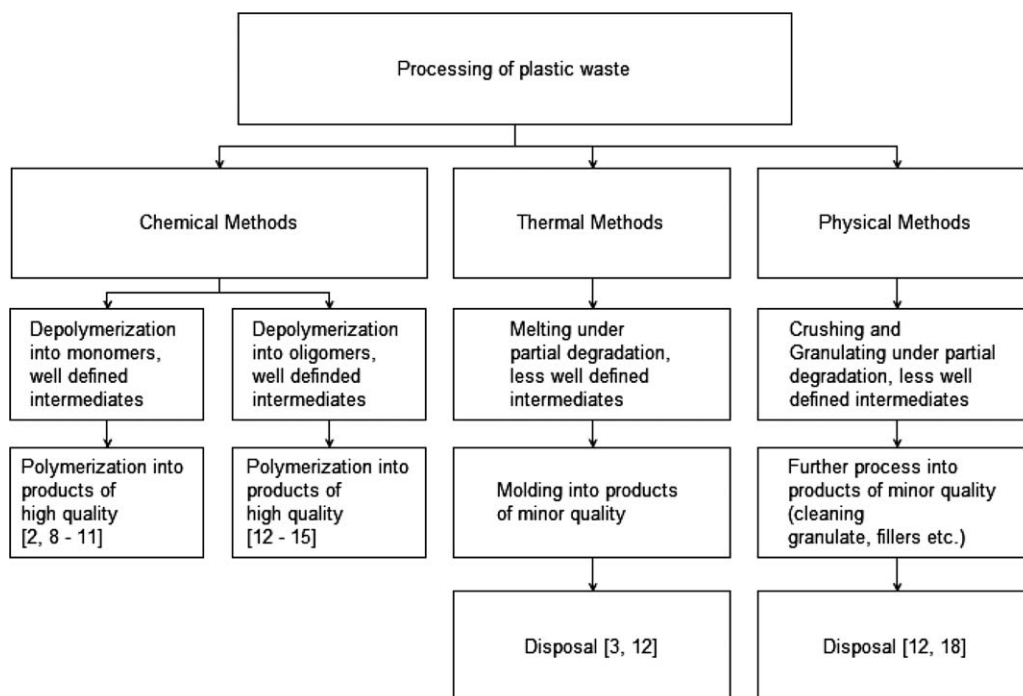


Figure 1. Examples of organic polymer waste recycling strategies.

building blocks. Such a pathway consists of: (a) defined decomposition of macromolecules into smaller fragments which can easily be purified like low molecular substances, followed by (b) purification using classical methods of chemical process engineering, and (c) subsequent repolymerization yielding materials that are suitable for high-quality products composed of second generation monomers.

In the present contribution, the defined decomposition of PET into tailored second-generation monomers is studied. Controlled PET degradation was performed via blocking chain scission.<sup>12,13</sup> While the ester linkages were cleaved during decomposition they were simultaneously masked by a blocking agent to prevent re-esterification. As blocking agents, adipic acid (AA), and trimellitic anhydride (TMA) were used and the influence of the amounts of AA and TMA used in the controlled degradation of PET was studied with respect to the oligomers produced. The general reaction sequence is depicted in Figure 2. Initially, one molecule AA reacts with the terminal hydroxy group of a polyester chain under formation of an AA ester blocked chain end (step A). In the next step, the polyester molecule is protonated at a random chain position (B) and the resulting protonated ester group undergoes acid-catalyzed polyester hydrolysis, steps B–E. The chain scission proceeds further upon subsequent esterification of the hydrolyzed fragments (F=A) and the chain degradation proceeds as long as there is AA available in the homogenous mixture.

According to the model of Taeger et al., who had studied the controlled breakdown of polyamide using TMA, the remaining polymerization degree of the obtained oligomers can be adjusted by appropriate selection of the amount of blocking agent used for depolymerization.<sup>12</sup> In the present study, this quantitative model was adapted and evaluated for its suitability in controlled PET depolymerization. The reaction products

were analyzed by infrared spectroscopy, differential scanning calorimetry (DSC), and <sup>1</sup>H-NMR-spectroscopy.

## EXPERIMENTAL

### Chemicals

PET Arnite® A04 900 from DSM Unlimited (Sittard, the Netherlands) with an average molecular weight of 75,533 g Mol<sup>-1</sup> was used. The degrading agents were AA and TMA from Acros Organics (Geel, Belgium). Defined polyethylene naphthalate (PEN) oligomers used for copolymerization with PET fragments were obtained by controlled degradation as described elsewhere.<sup>21</sup>

### Measurements

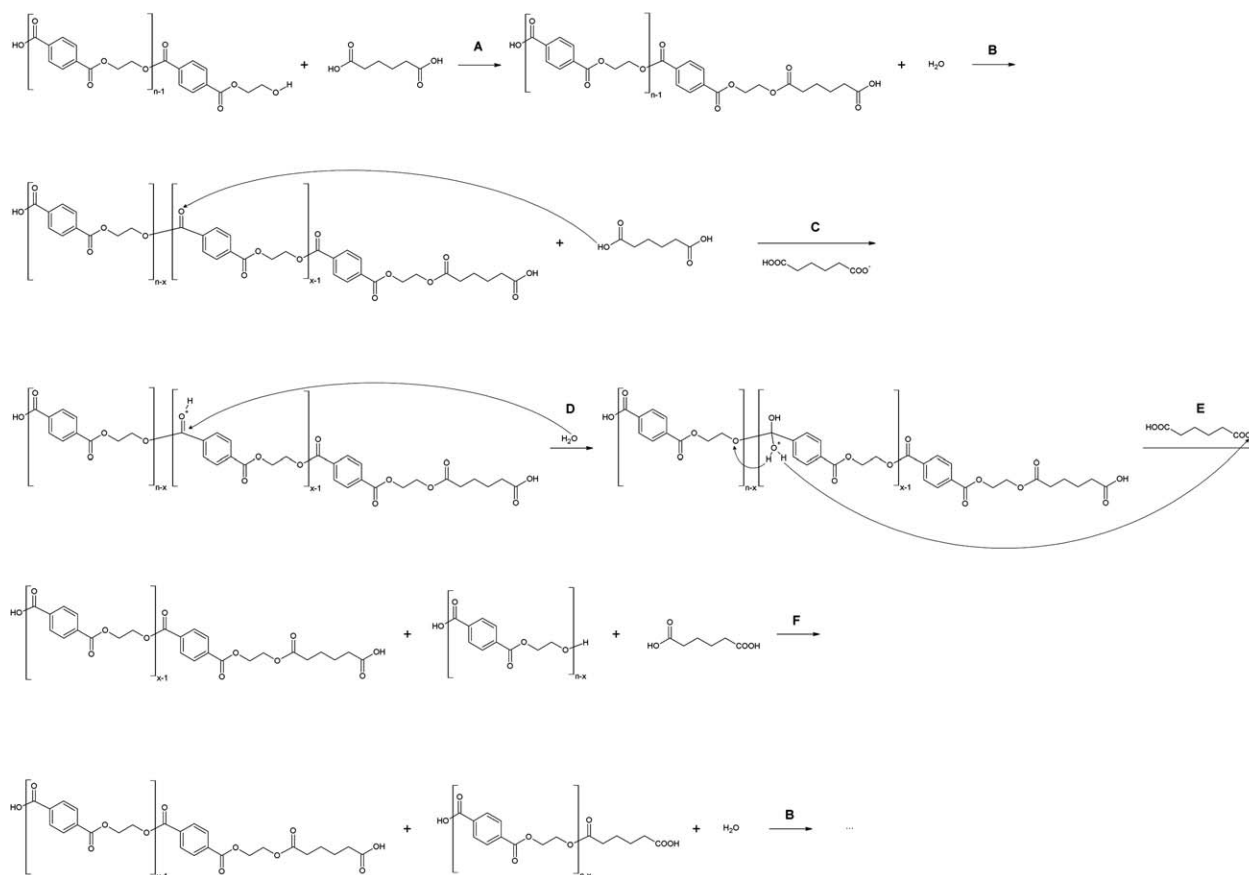
**Infrared Spectroscopy.** KBr-pellets were prepared from all samples (reference PET and degraded PET) and infrared spectra were recorded in transmission before and after PET degradation using a Spectrum One (Perkin Elmer LAS GmbH, Rodgau-Jüdisheim, Germany). Each sample was measured within a wavenumber range between 4000 and 450 cm<sup>-1</sup>. Each spectrum was averaged from four wavelength scans.

**Degradation Experiments.** Degradation experiments were performed with TMA and AA as the chain scission reagents. The stoichiometry for each experiment was determined based on the model developed by Taeger et al. by computing the targeted oligomer molecular weights in dependence of the amount of scission agent using the following equations<sup>4,5,11,12</sup>:

$$\bar{M}_{\text{Oligomer}} = \frac{m_{\text{PET}}}{m_{\text{DA}}} \cdot M_{\text{DA}} + M_{\text{DA}} \quad (1)$$

$$m_{\text{DA}} = \frac{m_{\text{PET}} \cdot M_{\text{DA}}}{\bar{M}_{\text{Oligomer}} - M_{\text{DA}}} \quad (2)$$

where  $\bar{M}_{\text{Oligomer}}$  is the molecular weight of the oligomer produced;  $M_{\text{DA}}$  is the molecular mass of degrading agent; and



**Figure 2.** Blocking chain scission of PET with adipic acid.

$m_{\text{PET}}$ ,  $m_{\text{DA}}$  are the masses of used polymer and degrading agent, respectively. The polymerization degree was obtained by dividing the molecular weight of an oligomer by the molar mass  $M_{\text{RU}}$  ( $192.12 \text{ g mol}^{-1}$ ) of the PET repeating unit [equation (3)]:

$$DP = \frac{\bar{M}_{\text{Oligomer}}}{M_{\text{RU}}} \quad (3)$$

A series of degradation experiments were performed by melt-mixing pulverized PET at  $270^\circ\text{C}$  under nitrogen atmosphere with varying concentrations of scission agent (approximately 2% and 10% w/w for TMA and 0.6–20% w/w for AA) that

were calculated to be suitable for the preparation of defined fragmentation products. Details are given in Table I.

Samples were taken at regular time intervals during the reaction for testing the completeness of conversion by thin layer chromatography (TLC). For this purpose, an aluminum oxide TLC plate with fluorescent indicator and ethanol as eluent was used. Samples were dissolved in hexafluoro-isopropanol, reprecipitated with ethanol and delivered onto the plate.

After the reactions were finished, the reaction mixtures were cooled to room temperature and the produced oligomer mixtures were ground to a fine powder in an analytical mill prior

**Table I.** Calculation of the Polymerization Degree in Dependence of Different Amounts of Chain Scission Agent<sup>12</sup>

Sample	Chain scission agent	Mass of PET (g)	Mass of scission agent (g)	Calculated DP <sup>a</sup>
1	TMA	37.75	0.80	50
2	TMA	37.75	3.75	10
3	AA	37.79	0.24	121
4	AA	37.66	0.39	74
5	AA	37.76	0.73	40
6	AA	37.69	1.57	19
7	AA	37.75	3.10	10
8	AA	37.53	6.78	5

<sup>a</sup>Theoretical degree of polymerization calculated according to eq. (3).

to examining the actual molecular weights obtained. The molecular weights were determined by <sup>1</sup>H-NMR-spectroscopy similar to the method described in.<sup>22–25</sup>

All reactions were finished after a reaction time of 2 hours after which time the polymerization degree did not change further and all of the AA had reacted as determined by TLC.

**Determination of the Molecular Weight of Oligomers.** To determine the degree of polymerization of the untreated and treated PET-samples, <sup>1</sup>H-NMR-spectra were recorded on a Bruker AC 250 NMR spectrometer at a magnetic field strength of 5.85 T (250.10 MHz for <sup>1</sup>H) at 27°C. The <sup>1</sup>H 90° pulse length was 9.6 μs, the spectral width was 4000 Hz. Samples were dissolved in a solution of deuterio trifluoroacetic acid and deuterio chloroform (1:1, v/v). Chemical shifts were reported relative to the residual proton of deuterio chloroform at 7.27 ppm.

For the determination of polymerization degrees in the AA blocked PET fragments, the peak area at a chemical shift of 1.72 ppm representing the aliphatic protons in β-position of the AA molecule, A<sub>H4</sub>, and the peak areas of the protons in the ethylene bridges of the PET chain (chemical shifts between 4.60 ppm to 4.84 ppm), A<sub>H2</sub>, were calculated. In Figure 9, the chemical structure of the partially degraded and AA-modified PET chain is given and the positions of the protons used for NMR analysis are indicated. As evident from Figure 9, the three peaks observed at chemical shifts 4.60, 4.69, and 4.84 ppm represent the four ethylene protons of one repeating unit that correspond to 4*n* protons in the polymer chain. The methylene protons in the β-position of an adjacent AA at 1.72 ppm correspond to four protons. Thus, by comparing the peak intensities, it is possible to determine the polymerization degree *n* of the fragmented PET-samples.

From the peak ratio A<sub>H2</sub>/A<sub>H4</sub> the number of repeating units (*n*) (the polymerization degree, DP) of the partly degraded products was calculated by using the following equation:

$$DP = n = \frac{A_{H2}}{A_{H4}} \quad (4)$$

In turn, the molecular weight was calculated by multiplying the polymerization degree with the molar mass of the repeating unit (192.17 g Mol<sup>-1</sup>).

For the determination of polymerization degrees in the TMA-blocked PET fragments, the peak area of the proton bound to the aromatic C-3 atom in the TMA molecule (chemical shift 8.63 ppm), A<sub>H3</sub>, was used and compared to the sum of the peak areas of the protons in the ethylene bridges of the PET chain (chemical shifts 4.60, 4.69, and 4.84 ppm), A<sub>H2</sub>.

**Preparation of Block-Copolyesters with Defined Block Length from Oligomeric PET.** Oligomeric PET with polymerization degrees of either 5 (abbreviated in the following text as “PET5”) or 40 (abbreviated in the following text as “PET40”) was melt-mixed at 260°C with PEN of polymerization degree 5 (abbreviated in the following text as “PEN5”) under nitrogen atmosphere in a molar ratio of 1:1. After 10 minutes, the reaction mixtures were cooled to room temperature still under nitrogen and milled before block length and degree of randomness of the

obtained copolymers were determined. As prolonged melt-mixing of PET and PEN species leads to the formation of random copolyesters because of advanced transesterification<sup>26</sup> the same composition of PET- and PEN-oligomers was mixed in the melt for 20 minutes to compare thermal properties of random and block copolyesters.

The resulting block copolyesters were named after the used oligomer fragments. Hence, the block copolymer that was prepared from polyethylene terephthalate oligomer with a polymerization degree of 5 reacted and a PEN oligomer with a polymerization degree of 40 was called PET5PEN40.

The average number of repeating units of each polyester species comprising the copolyester is denoted as the block length of each respective polyester species. Hence, the block lengths of PET segments (LnPET) and PEN segments (LnPEN) in the novel copolyester were determined by evaluating the areas of the ethylene peaks in the <sup>1</sup>H-NMR-spectra originating from the ethylene units of PET (A<sub>TET</sub>, peak G, Figure 10), of PEN (A<sub>NEN</sub>, peak A, Figure 10) and of ethylene units between terephthalic and naphthalic units (A<sub>NET</sub>, peak E, Figure 10) [eqs. (5) and (6)].<sup>26</sup>

$$LnPET = \frac{A_{NET} + 2A_{TET}}{A_{NET}} \quad (5)$$

$$LnPEN = \frac{A_{NET} + 2A_{NEN}}{A_{NET}} \quad (6)$$

Additionally, the degree of randomness (RD) was calculated from the <sup>1</sup>H-NMR-data [eq. (7)] to decide whether the copolyester is a random copolymer (RD = 1), an alternating copolymer (RD = 2), a physical blend (0 < RD < 1) or a block copolymer (0 < RD < 1):<sup>26</sup>

$$RD = \frac{1}{LnPET} + \frac{1}{LnPEN} \quad (7)$$

The degree of randomness is derived from the sequence lengths of the PET and PEN blocks in the PET-PEN-copolyester and indicates the statistical distribution of PET- and PEN-segments in the polymer chain. A low value of the RD indicates a block copolymer while a high value of the RD indicates a random-copolymer.

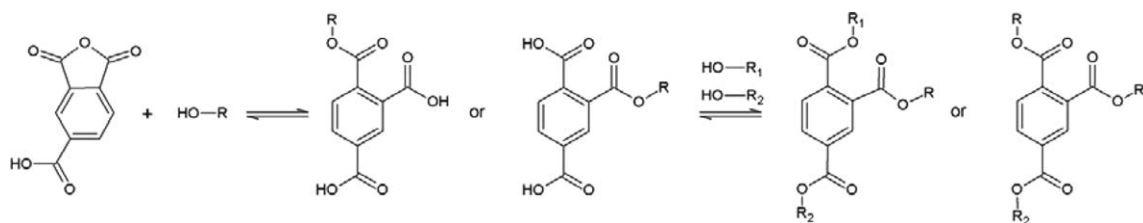
**Differential Scanning Calorimetry.** Thermal properties of oligomers obtained from PET fragmentation and copolymers of PET oligomers with PEN were studied by DSC using a DSC 204 F1 Phoenix (Netzsch GmbH; Selb, Germany). Samples of 10 mg were weighed into aluminum crucibles (40 μL) with pierced lid and subjected to a dynamic temperature program (heating rate: 20 K/min, temperature range from 20°C to 300°C) under nitrogen atmosphere. The obtained thermograms were analyzed using the computer software Proteus—Thermal Analysis Version 4.8.3 (Netzsch GmbH; Selb, Germany).

In case of the analysis of copolymers, DSC was also used to investigate the polymer phase homogeneity.

## RESULTS AND DISCUSSION

### Degradation of PET with Trimellitic Anhydride

As polyamides (PA) have already successfully been degraded to defined oligomers using TMA and the molecular weight of the



**Figure 3.** Hydrolysis of TMA with alcoholic hydroxyl groups, followed by esterification of carboxy groups.

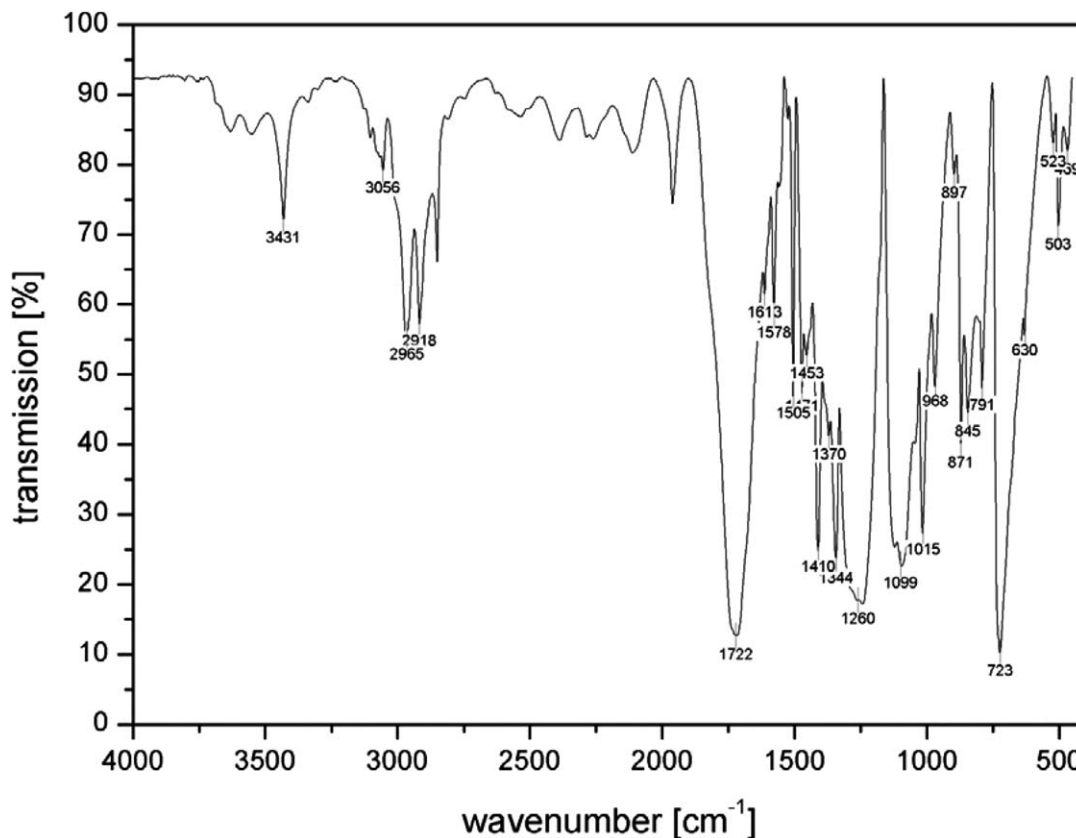
formed PA oligomers showed good quantitative correlation with the used concentrations of the scission agent, in a first set of experiments, TMA was tested as a scission agent for the partial degradation of PET into defined fragments.

In an attempt to produce oligomeric PET with polymerization degrees of 10 and 50, 37.75 g PET were mixed in the melt with either 3.75 or 0.8 g of TMA as suggested by eq. (2). As indicated by NMR spectroscopy it was found that under the reaction conditions applied, degradation of PET took place. However, when the molecular weight of the resulting oligomers was determined, significant deviations from the targeted values were observed. While eq. (3) predicted a remaining polymerization degree of 10, for the actually formed oligomer an experimental value of 20 was calculated from the <sup>1</sup>H-NMR signals. Similarly, a much higher remaining polymerization degree of 80 was found instead of the targeted value of 50 for the oligomer that had been treated with 0.8 g of TMA.

These results show that although TMA supported the reduction in molecular weight of PET, it was not suitable for degrading PET into defined oligomers when the model by Taeger et al. was applied.<sup>12</sup> No linear correlation between oligomer molecular weight and scission agent concentration was observed.

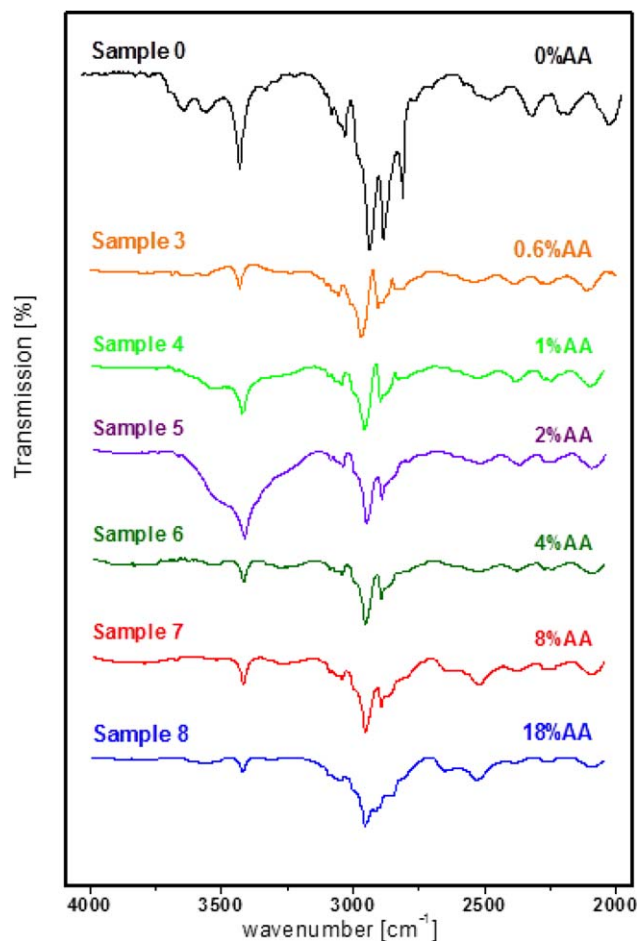
A possible reason for this could be the formation of branched structures in the course of the degradation process of PET. In the presence of alcohols, TMA hydrolyses to trimellitic acid.<sup>27</sup> As a trifunctional molecule, trimellitic acid may serve as a center for dendrimeric growth upon further reaction. Therefore, the three carboxy-groups present in hydrolyzed TMA may act as a crosslinking agent upon reaction with free hydroxyl groups of different PET chains yielding star-like ester-compounds with a TMA-molecule in the center. The possibility of forming such branched structures has been discussed in Ref. 27 and is shown in Figure 3.

In further experiments, TMA was substituted by AA which should not be able to form such star-shaped structures and



**Figure 4.** IR-spectrum of pure PET Arnite® A04 900.





**Figure 5.** Infrared spectra of the pure PET-sample (Sample 0, 0% AA) and of the PET samples 3–8 modified with varying concentrations of chain scission agent adipic acid of 0.6–18% in the wavenumber range from 3650 to 2850  $\text{cm}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

hence should yield defined concentration dependence of the degradation products.

#### Degradation of PET with Adipic Acid

**Qualitative Changes in the Molecular Structure.** In case of PET fragmentation with AA, PET samples were mixed in the melt under nitrogen flow with different amounts of the acid, which are listed in Table I. Samples were taken after 2, 3, and 4 hours for testing the completeness of the reaction.

The structural changes of PET that had occurred upon reaction with AA were studied by infrared spectroscopy. The spectrum of the unmodified starting material is shown in Figure 4; the spectra of the partly degraded samples are summarized in Figures 5 and 6. The IR-absorption bands of PET were assigned to the characteristic molecular group vibrations and are summarized in Table II.<sup>28–32</sup>

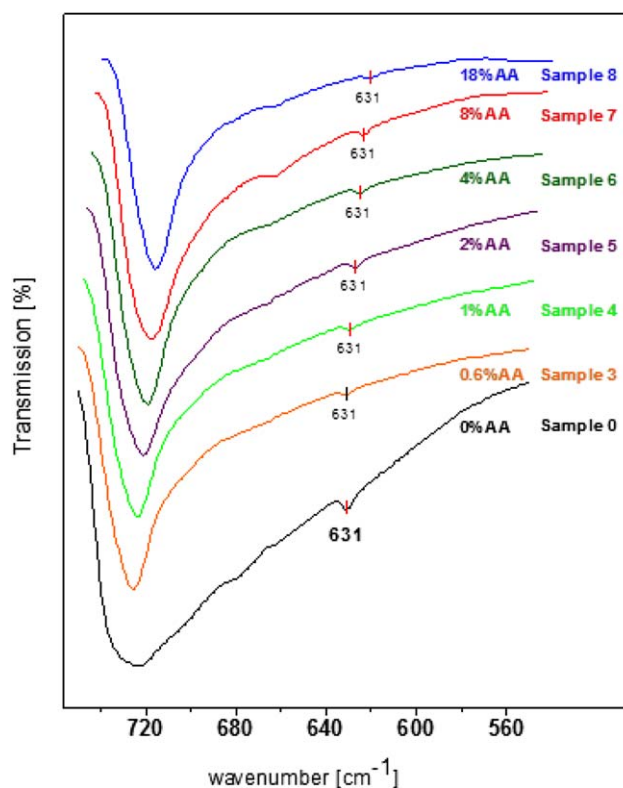
The IR-spectra of the partially degraded PET samples were compared to the spectrum of pure PET (Sample 0) to detect significant spectral changes caused by the fragmentation. Several differences in distinct spectral regions are apparent (Figure 5).

With the partly degraded samples, absorbance in the wavenumber ranges from 3650 to 2850  $\text{cm}^{-1}$ , from 3630 to 3430  $\text{cm}^{-1}$ , and from 3054 to 2850  $\text{cm}^{-1}$  m have all lost considerably in intensity compared to the spectrum of unmodified PET. The spectral changes at these wavelengths were more pronounced the more scission agent was used.

As the absorbance peaks at 3551 and 2966  $\text{cm}^{-1}$  as well as 2916  $\text{cm}^{-1}$  correspond to vibrations of hydroxyl groups and ethylene-bridges, Figure 5 indicates that the number of hydroxyl groups and ethylene bridges had decreased upon reaction of PET with AA as expected.

Moreover the absorption band at 631  $\text{cm}^{-1}$  of the deformation vibration of the  $\begin{matrix} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{C}- \end{matrix}$  ester-bond has almost disappeared, which indicates a reduction in the number of ester-linkages (Figure 6).

**Thermal Properties.** The effect of controlled degradation on the thermal properties of PET oligomers was studied by dynamic DSC.<sup>33</sup> The resulting melting peaks and reaction enthalpies of each sample, including original PET, are illustrated in Figures 7 and 8. The dependence of the melting peak temperature on the concentration of AA is obvious: the lowest melting temperature of 213.2°C was observed with the PET sample that was modified by 18% of AA (Sample 8). The highest melting temperature was observed with pure PET at 256.1°C (Sample 0) (Figure 7). The melting peak temperatures of the oligomeric



**Figure 6.** IR-absorptions at 631  $\text{cm}^{-1}$  of pure PET (0%AA) and samples 3–8 corresponding to concentrations of adipic acid from 0.6% to 18%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

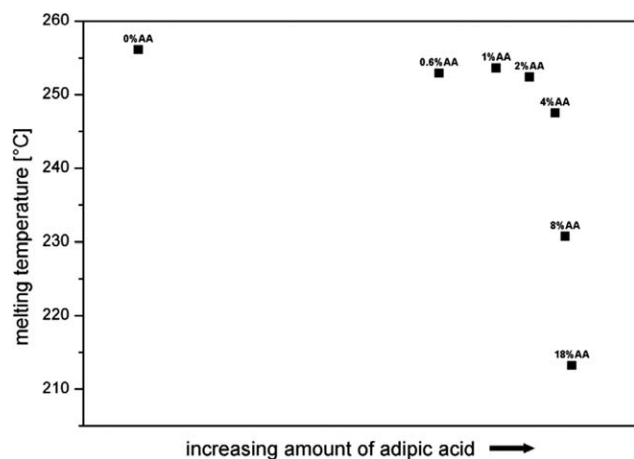


Figure 7. Dependence of melting peak temperature on amount adipic acid.

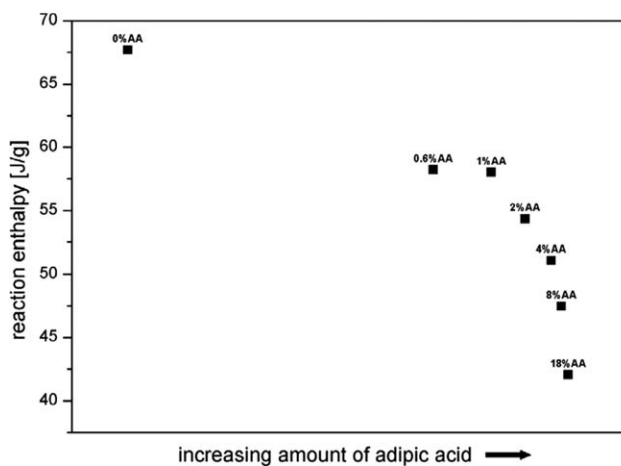


Figure 8. Reaction enthalpy versus increasing amount of adipic acid.

Table II. Assignments of IR-Absorptions of PET Arnite® A04 900<sup>28–32</sup>

Wavenumber (cm <sup>-1</sup> )	Assignment <sup>a–g</sup>
3551	$\nu(\text{OH})$
3430	Carbonyl overtone vibration
3054	$\nu(\text{CH})$ Phenyl-H-Atom
2966	$\nu_{\text{as}}(\text{CH}_2)$
2916	$\nu_{\text{s}}(\text{CH}_2)$
1723	$\nu(\text{C}=\text{O})$
1613	$\nu(\text{Phenylring})$
1578	$\nu(\text{Phenylring})$
1505	$\nu(\text{Phenylring})$
1472	$d(\text{CH}_2)$ (trans-conformation)
1454	$d(\text{CH}_2)$ (gauche-conformation)
1411	Phenylring (in-plane)
1370	$\omega(\text{CH}_2)$ (gauche-conformation)
1344	$\omega(\text{CH}_2)$ (trans-conformation)
1261	$\nu(\text{C}-\text{O})$
1099	$\nu(\text{C}-\text{O})$ (gauche-conformation)
1016	$d(\text{CH}_2)$
969	$\nu(\text{C}-\text{O})$ (trans-conformation)
897	$r(\text{CH}_2)$ (gauche-conformation)
871	$\gamma(\text{CH})$ Phenyl-H-Atom
844	$r(\text{CH}_2)$ (trans-conformation)
791	Phenylring (in-plane)
723	$\gamma(\text{CH})$ Phenyl-H-Atom
631	$d(\text{C}-\text{O}-\text{C})$
522	
503	$\gamma(\text{C}=\text{O})$
469	

<sup>a</sup>  $\nu$ : stretching vibration.

<sup>b</sup>  $\nu_{\text{as}}$ : asymmetrical stretching.

<sup>c</sup>  $\nu_{\text{s}}$ : symmetrical stretching.

<sup>d</sup>  $d$ : in-plane deformation vibration.

<sup>e</sup>  $\omega$ : wagging.

<sup>f</sup>  $r$ : rocking vibration.

<sup>g</sup>  $\gamma$ : out-of-plane deformation vibration.

PET fragments show a steady increase with decreasing amounts of AA (Samples 7–4). The differences in the melting peaks of PET oligomers which were produced with smaller quantities of AA (0.6%, 1%, and 2%) are much less pronounced and the values are close to that of unmodified PET. This observation is because of the experimental difficulty in distinguishing polymers of rather high molecular weights satisfactorily well by their melting points in DSC. With high molecular weight polymers, the differences in molecular weights are much less significant relative to their total molecular weight and the trend of melting temperatures displays an asymptotic behavior towards higher molar masses.<sup>4,32–36</sup> Hence, only the polymer fragments of lower molecular weights can be distinguished sufficiently well by their melting temperatures. The observed series of increasing melting points corresponds well with a series of PET oligomers of increasing molecular weights and supports the hypothesis that the oligomer molecular mass is strongly affected by the amount of scission agent used.

Furthermore, the reaction enthalpy shows a similar trend in dependence of the amount of AA used. The lowest reaction enthalpy of  $42.05 \text{ J g}^{-1}$  was observed for the PET sample degraded by 18% AA; the samples treated with lower amounts show increasing reaction enthalpies with decreasing amount of used AA. As in the case of the melting temperatures, the highest values for the reaction enthalpy were found with the unmodified PET ( $67.70 \text{ J g}^{-1}$ , see also Figure 8).

These results suggest already different degrees of degradation in the samples. To provide quantitative evidence, in the next step, the actual molecular masses of the oligomeric PET fragments were determined and compared to the predicted values as calculated by eq. (3).

**Determination of the Polymerization Degree.** NMR-recordings were taken for the basic characterization of pure PET and AA as well as for the determination of the polymerization degree of the oligomeric degradation products. The chemical shifts of the partly degraded PET samples are listed in Table III. The chemical structure of the oligomeric units, the <sup>1</sup>H-NMR spectrum and the peak assignment are illustrated in Figure 9.

From the integration ratio  $A_{\text{H}_2}/A_{\text{H}_4}$ , the resulting polymerization degrees of the samples were determined and compared to

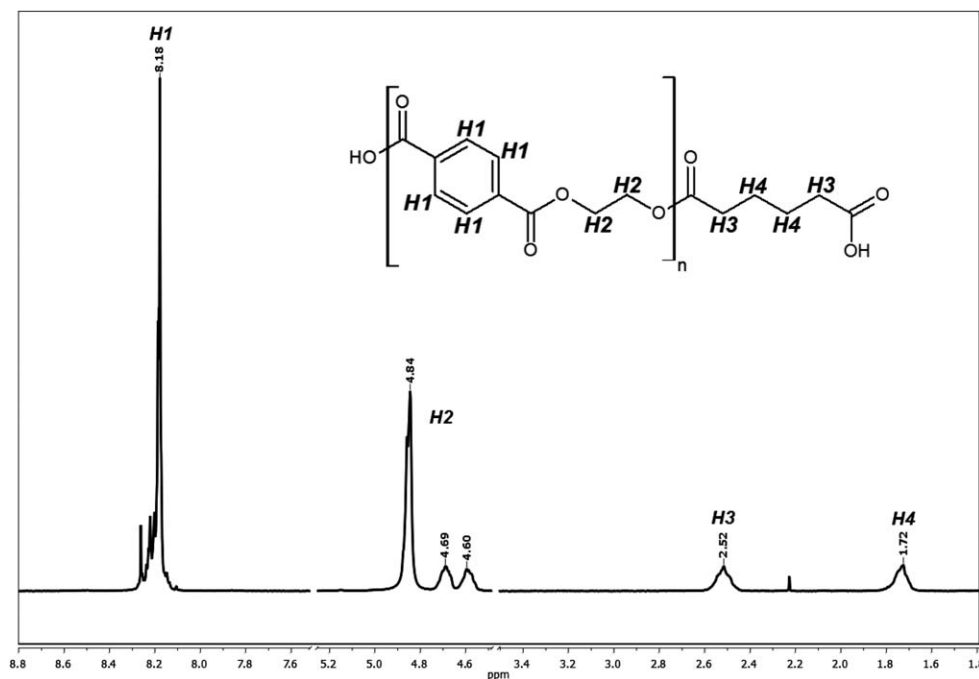


Figure 9. <sup>1</sup>H-NMR-spectrum and peak assignments of the characteristic protons in PET-oligomer degraded with adipic acid.

the calculated polymerization degrees as predicted by eq. (3).<sup>22–25</sup> Table IV lists the predicted and the observed polymerization degrees as well as the corresponding molecular

weights of all samples. All observed polymerization degrees of the samples prepared were in good agreement with the used model.

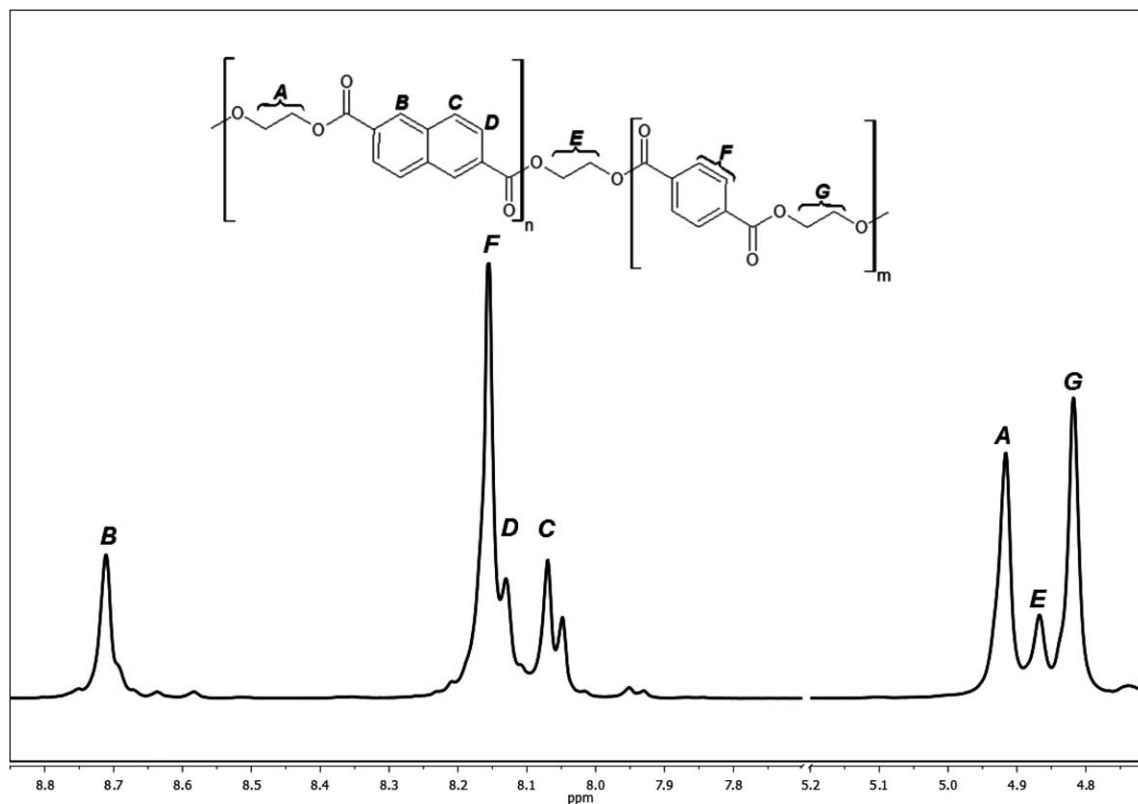


Figure 10. <sup>1</sup>H-NMR-spectrum and peak assignments of the characteristic protons in PET-PEN-co-polyester from defined oligomers degraded by adipic acid.



**Table III.** Chemical Shifts in ppm of Pure PET (0%AA), Adipic Acid, Oligomeric Degradation Products and Peak Areas of Characteristic Protons

Sample <sup>a</sup>	Chemical shift $\delta$ in ppm			
	H1	H2	H3	H4
<b>Adipic acid</b>	-	-	2.40	1.63
<b>0</b>	8.17	4.83-4.56	-	-
<b>3</b>	8.17	4.83-4.56	2.51	1.73
<b>4</b>	8.14	4.80-4.53	2.48	1.69
<b>5</b>	8.18	4.85-4.57	2.52	1.73
<b>6</b>	8.16	4.83-4.56	2.50	1.71
<b>7</b>	8.07	4.68-4.43	2.36	1.60
<b>8</b>	8.15	4.81-4.56	2.49	1.72

<sup>a</sup> **0**: PET without adipic acid (0%AA), **3**: PET with 0.6%AA, **4**: PET with 1%AA, **5**: PET with 2%AA, **6**: PET with 4%AA, **7**: PET with 8%AA, **8**: PET with 18%AA.

### Application of Building Blocks in Novel Block Copolymers

Although much research work is dedicated to the controlled synthesis of defined block copolymers with tailored structure and architecture,<sup>37-39</sup> the majority of papers deals with the synthesis of random copolymers starting from monomers.<sup>40-49</sup> The preparation of PET-PEN-copolyesters, too, is mainly accomplished using monomers such as, for example 1,4-dimethylterephthalate, 2,6-dimethylnaphthalate, and ethylene glycol, and producing random copolyesters.<sup>44,50-53</sup> Alternatively, PET-PEN copolyesters were also prepared applying undefined oligomers leading to undefined block copolymers or even random copolyesters.<sup>54</sup>

In contrast, the experimental strategy followed in this article focuses on the possibility of preparing well-defined block copolyesters by the application of building blocks of defined structure.

In comparison to random copolymers block copolymers typically possess superior thermal properties such as, for example, higher melting temperatures and higher glass transition temperatures leading to enhanced thermal stability.<sup>55-58</sup> The superior properties of defined block copolymeric structures are frequently used within the concept of self-reinforcing polymers. Such materials display, for example, much improved gas barrier properties.<sup>58</sup>

In this section, the thermal properties of novel block copolymers obtained from defined PET and PEN oligomers are described and compared to the thermal properties of random copolymers from the same oligomers. The evidence for block-copolymer formation and determination of the block length of the products obtained by melt-mixing oligomeric PET with oligomeric PEN was conducted with <sup>1</sup>H-NMR and DSC. The chemical shifts of the characteristic peaks (ethylene units of PEN, PET, and ethylene units between terephthalic and naphthalic groups, respectively, peaks A, G, E, Figure 10) are given in Table V.

With the corresponding integrated intensities (Table VI) the lengths of PET/PEN segments as well as the degree of

**Table IV.** Theoretical and Practical Polymerization Degrees and Resulting Molecular Weight of Degraded Products

Sample <sup>a</sup>	Predicted DP <sup>b</sup>	Observed DP <sup>c</sup>	$M_n^d$ (g/mol)
<b>3</b>	121	122	23,445
<b>4</b>	74	73	14,028
<b>5</b>	40	43	8263
<b>6</b>	19	20	3843
<b>7</b>	10	10	1922
<b>8</b>	5	5	961

<sup>a</sup> PET-oligomers obtained from PET mixed with various concentrations of adipic acid: **3**: 0.6%, **4**: 1%, **5**: 2%, **6**: 4%, **7**: 8%, **8**: 18%.

<sup>b</sup> Theoretical degree of polymerization calculated according to eq. (3).

<sup>c</sup> Degree of polymerization from NMR measurements.

<sup>d</sup> Molecular weight determined with eq. (3).

randomness were calculated as described in the experimental part. As seen in Table VI, the design of a block-copolyester with defined PET/PEN-sequence lengths resulting from the reaction of oligomers with defined polymerization degree was successfully conducted. The degree of randomness (0.39 for the PET5PEN5 and 0.21 for the PET40PEN5 copolymer) also indicates a block-copolymer character.<sup>26,33,60-62</sup>

In contrast, the melt-mixing under prolonged reaction time favored the formation of random copolymers as indicated by the degrees of randomness close to one (PET5PEN5rand: 0.93 and PET40PEN5rand: 0.96) obtained for the reaction products.

To distinguish between blending and actual copolymer formation in the case of the block copolymers, thermal analysis of the condensation products was performed. DSC indicated the formation of real copolymers. The thermograms of the samples show in each case a single glass transition temperature (Table VI), proving that the samples are not physical blends.<sup>63</sup> Additionally, the glass transition temperatures of PET5PEN5 (T<sub>g</sub> 59.40°C) and PET40PEN5 (T<sub>g</sub> 77.10°C) are higher in comparison to the single oligomers PET5 (T<sub>g</sub> 48.95°C), PET40 (T<sub>g</sub> 60.85°C) and PEN5 (T<sub>g</sub> 50.95°C). Obviously, PEN5 increases the glass transition temperatures of both block copolyesters resulting from the rigidity of the introduced naphthalene units. PET5PEN5 copolymerization yielded completely amorphous polyester with a glass transition temperature at ca. 59°C but with no visible melting or crystallization peaks in the DSC thermogram. In case of PET40PEN5 a semicrystalline polyester was

**Table V.** Chemical Shifts in ppm of Ethylene Units from PEN (A), PET (G) and Ethylene Units between Terephthalic and Naphthalic Groups (E) in Copolyester Samples

Sample	Chemical shift $\delta$ in ppm		
	A	E	G
<b>PET5PEN5</b>	4.95	4.89	4.84
<b>PET40PEN5</b>	4.90	4.84	4.79
<b>PET5PEN5rand</b>	4.94	4.89	4.83
<b>PET40PEN5rand</b>	4.94	4.89	4.83

**Table VI.** Integrated Intensities of Ethylene Units from Peaks A, E, G, and Resulting Sequence Lengths of PET Segment and PEN Segment; Including Glass Transition, Melting, and Crystallization Temperatures of Copolyester Samples

Sample	$A_{\text{NEN}}$	$A_{\text{NET}}$	$A_{\text{TET}}$	$\text{LnPET}$	$\text{LnPEN}$	RD	$T_g^a$ [°C]	$T_m^b$ [°C]	$T_c^c$ [°C]
<b>PET5PEN5</b>	1.74	1.00	2.34	5.68	4.48	0.39	59.40	-	-
<b>PET40PEN5</b>	2.15	1.00	19.40	39.80	5.30	0.21	77.10	240.83	200.80
<b>PET5PEN5rand</b>	0.56	1.00	0.52	2.04	2.12	0.96	47.80	-	-
<b>PET40PEN5rand</b>	0.45	1.00	0.74	2.48	1.90	0.93	65.80	229.60	184.10

<sup>a</sup>Glass transition temperature.<sup>b</sup>Melting temperature.<sup>c</sup>Crystallization temperature.

obtained with a glass transition temperature at 77.1°C, a melting temperature at 240.83°C and a crystallization temperature of 200.80°C (Table VI). These differences in thermal behavior can be explained by the introduction of the more rigid naphthalene aromatic structure into the polyester backbone. It is evident from Table VI that the novel block copolyester shows an improved softening behavior as compared to the random copolymer (indicated by the higher glass transition temperatures of both the PET40PEN5 and PET5PEN5 block copolymers). Hence, the design of defined oligomers by controlled degradation of used PET samples using a chain scission agent leads to building blocks allowing the synthesis of block copolymers with improved thermal performance.

However, besides the thermal properties, the interfacial properties of the copolymer play an important role in the processing of such materials as well. Especially in the case of PET and PEN, which are not miscible in an unmodified state<sup>59</sup>, by creating block copolymers of defined sequence lengths, it should be possible to control the relative surface energy difference between these two polymers and hence to control mixing and formation of a stable blend between PET and PEN. Such blends are of interest as encapsulating or packaging materials. Based on the present experimental strategy of generating defined oligomers for novel block copolymers a related study, the interfacial properties of defined PET-PEN block copolymers will be covering these interfacial aspects in detail.<sup>21</sup>

## CONCLUSION

Degradation experiments were performed to prepare oligomeric PET building blocks of defined composition using the model by Taeger et al.<sup>12</sup> It was found that while TMA did not result in oligomers of molecular weight according to the model calculation with AA as chain scission agent oligomers of defined polymerization degrees could be prepared. The method used for depolymerization in this study proved to be readily applicable and the procedure could easily be transferred to industrial scale equipment in reactive extrusion or standard batch processes. It requires only moderate consumption of chemicals, subjects the waste material to comparatively mild degradation conditions and yields relatively low residual contamination by solvent or monomer molecules. It was shown that it is possible to design oligomeric ethylene terephthalate building blocks with defined molecular weights. These defined oligomeric products were used to design a new block copolyester containing PET

segments and PEN segments of characteristic sequence lengths. The designing of block copolyesters with segments of specific block length shows the applicability of tailored second-generation oligomers to produce novel polymers with specific properties that are not necessarily inferior to polymers based on first-generation monomers. For instance, in the present study, the thermal properties of the resulting block-copolymers was improved (enhanced glass transition temperature) by using recycled oligomers. Hence, the method seems suited for the synthesis of special materials like encapsulants or packaging materials and for the design of specific properties such as tailored interfacial behavior for improved compatibility in blends. In a subsequent study, the surface energy of PET and PEN block copolymers was tailored by preparing designed oligomers of defined polymerization degree and linking them to block copolyesters of defined sequence length composition.

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## ABBREVIATIONS

A	Absorption
AA	Adipic acid
$A_{\text{NEN}}$	integrated intensity of ethylene units from PEN
$A_{\text{NET}}$	integrated intensity of ethylene units between terephthalic and naphthalic groups
$A_{\text{TET}}$	integrated intensity of ethylene units from PET
d	in-plane deformation vibration
DP	Degree of polymerization
$\text{LnPEN}$	block length of ethylene naphthalate units
$\text{LnPET}$	block length of ethylene terephthalate units
$M_{\text{DA}}$	molar mass of degrading agent
$m_{\text{DA}}$	mass of degrading agent
mg	Milligramm
MHz	Megahertz
$M_n$	number average molecular weight
PET	Polyethylene terephthalate
PEN	Polyethylene naphthalate
ppm	parts per million

r	rocking vibration
RD	degree of randomness
TMA	trimellitic anhydride
$\gamma$	out-of-plane deformation vibration
$\delta$	chemical shift in ppm
$\nu$	stretching vibration
$\nu_{as}$	asymmetrical stretching
$\nu_s$	symmetrical stretching
$\omega$	wagging

## REFERENCES

- Baliga, S.; Wong, W. T. *J. Polym. Sci. A Polym. Chem.* **1989**, *27*, 2071.
- Paszun, D.; Spychaj, T. *Ind. Eng. Chem. Res.* **1997**, *36*, 1373.
- Yamaye, M.; Hashime, T.; Yamamoto, K.; Kosugi, Y.; Cho, N.; Ichiki, T.; Kito, T. *Ind. Eng. Chem. Res.* **2002**, *41*, 3993.
- Pitav, J. GB Patent 822,834, November 4, **1959**.
- Nikles, D. E. *Macromol. Mater. Eng.* **2005**, *290*, 13.
- Shah, R. V.; Borude, V. S.; Shukla, S. R. *J. Appl. Polym. Sci.* **2012**, DOI: 10.1002/APP.37900.
- Firas A., Dumitru, P. *Eur. Polym. J.* **2005**, *41*, 1453.
- Chen, J. Y.; Ou, C. F.; Hu, Y. C.; Lin, C. C. *J. Appl. Polym. Sci.* **1991**, 1501.
- Ruvolo-Filho, A.; Curti, P. *Ind. Eng. Chem. Res.* **2006**, *45*, 7985.
- Shah, R. V.; Shukla, S. R. *J. Appl. Polym. Sci.* **2012**, *125*, 3666.
- Khalaf, H. *Chem. Eng. J.* **2012**, *192*, 45.
- Taeger, E.; Mertel, H.; Meusel, E.; Riedel, B. Müller, W. *Chemiefasern/Textilindustrie* **1993**, *43/95.*, 525.
- Eichhorn, K. -J.; Lehmann, D.; Voigt, D. *J. Appl. Polym. Sci.* **1996**, *62*, 2053.
- Lehmann, D. DD Patent 276,290, February 21, **1990**.
- Chen, -I. L. U.S. Patent 4,379,912, April 12, **1983**.
- Parab, Y. S.; Pingale, N. D.; Shukla, S. R. *J. Appl. Polym. Sci.* **2012**, *125*, 1103.
- Issam, A. M.; Hena, S.; Khizrien, A. K. N. *J. Polym. Environ.* **2012**, *20*, 469.
- Datye, K. V.; Raje, H. M.; Sharma, N. D. *Resour. Conserv.* **1984**, *11*, 117.
- Minoru, G.; Tomoko, I.; Mitsuru, S.; Motonobu, G.; Hirose, T. *Ind. Eng. Chem. Res.* **2005**, *44*, 3894.
- Yoshioka, T.; Sato, T.; Okuwaki, A. *J. Appl. Polym. Sci.* **1994**, *52*, 1353.
- Geyer, B.; Röhner, S.; Lorenz, G.; Kandelbauer, A. *J. Appl. Polym. Sci.* (manuscript in preparation)
- Baldissera, A.; Valério, C. E. S.; Basso, N. R. de S.; Guaragna, F.; Einloft, S.; Tessier, M.; Fradet, A. *Quim. Nova* **2005**, *28*, 188.
- Charlier, Y.; Godard, P.; Daoust, D.; Strazielle, C. *Macromolecules* **1994**, *27*, 3604.
- Li, H.; Jackson, A. B.; Kirk, N. J.; Mauritz, K. A.; Storey, R. F. *Macromolecules* **2011**, *44*, 694.
- Saint-Loup, R.; Robin, J.-J.; Boutevin, B. *Macromol. Chem. Phys.* **2003**, *204*, 970.
- Kim, S. H. In *Modern Polyesters*; Scheirs, J., Long, T. E., Eds.; Wiley: Chichester, West Sussex, **2003**; Chapter 20, p 673.
- Puskas I.; Fields, E. K. *Ind. Eng. Chem. Prod. Res. Develop.* **1970**, *9*, 403.
- Hummel, D.O.; Scholl, F. In *Atlas der Polymer- und Kunststoffanalyse*; Hummel, D. O., Eds.; Carl Hanser Verlag: München, **1984**; Vol. 1, Chapter 1, p 158.
- Tadokoro, H.; Tatsuka, K.; Murahashi, S. *J. Polym. Sci.* **1962**, *59*, 413.
- Grime, D.; Ward, I. M. *Trans. Faraday Soc.* **1958**, *54*, 959.
- Daniels, W. W.; Kitson, R. E. *J. Polym. Sci.* **1958**, *23*, 161.
- Liang, C. Y.; Krimm, S. *J. Mol. Spectrosc.* **1959**, *3*, 554.
- Frick, A.; Stern, C. In *DSC-Prüfung in der Anwendung*; Hanser-Verlag: München, Wien, **2006**, Chapter 3, p 74.
- Pielichowski, K.; Flejtuch, K. *Polym. Adv. Technol.* **2002**, *13*, 690.
- Fatou, J. G.; Mandelkern, L. *J. Phys. Chem.* **1965**, *69*, 417.
- Stack, G. M.; Mandelkern, L. *Macromolecules* **1984**, *17*, 321.
- Dung, B. T. New segmented block copolymers based on hard and soft segments using selectively reacting bifunctional coupling agents. Ph.D. Thesis, Dresden University of Technology, Dresden, Sachsen, February 2007.
- Hilf, S.; Klos, J.; Char, K.; Woo, H.; Kilbinger, A. F. M. *Macromol. Rapid Commun.* **2009**, *30*, 1249.
- Zhu, X.; Traub, M. C.; Vanden Bout, D. A.; Plunkett, K. N. *Macromolecules* **2012**, *45*, 5051.
- Watanabe, Y.; Shirahama, H.; Yasuda, H. *React. Funct. Polym.* **2004**, *59*, 211.
- Zhang, Y.; Zengguo, F.; Qingling, F.; Fuzhai, C. *Polym. Degrad. Stabil.* **2004**, *85*, 559.
- Kyeremateng, S. O.; Amado, E.; Kressler, J. *Eur. Polym. J.* **2007**, *43*, 3380.
- Berti, C.; Celli, A.; Marchese, P.; Barbiroli, G.; Di Credico, F.; Verney, V.; Commereuc, S. *Eur. Polym. J.* **2008**, *44*, 3650.
- Zo-Chun, J. (Nan Ya Plastics Corp.). DE 601,19,293, September 28, **2006**.
- Kobayashi, S.; Kataoka, H.; Ishizone, T.; Kato, T.; Ono, T.; Kobukata, S.; Arimoto, K.; Ogi, H. *React. Funct. Polym.* **2009**, *69*, 409.
- Nguyen, M. N.; Bressy, C.; Margailan, A. *Polym.* **2009**, *50*, 3086.
- Hayden, P.; Roberts, R. *Int. J. Appl. Radiat. Isot.* **1960**, *7*, 317.
- Weiser, M. S.; Thomann, Y.; Heinz, L. -C.; Pasch, H.; Mühlhaupt, R. *Polymer* **2006**, *47*, 4505.
- Cureton, L.; Turner, S. *Eur. Polym. J.* **2011**, *47*, 2303.
- Shemper, B.; Mathias, L. *Eur. Polym. J.* **2004**, *40*, 651.
- Lu, T. -S.; Sun, Y. -M.; Wang, C. -S. *J. Polym. Sci.* **1995**, *33*, 2841.
- Ahn, T. H.; Park, Y. H.; Kim, S. H.; Baik, D. H. *J. Appl. Polym. Sci.* **2003**, *90*, 3473.

53. Lu, X.; Windle, A. H. *Polymer*. **1995**, *36*, 451.
54. Lu, X.; Windle, A. H. *Polymer* **1996**, *37*, 2027.
55. James, N. R.; Ramesh, C.; Swaminathan, S. *Macromol. Chem. Physic.* **2001**, *202*, 2267.
56. Wang, Z.; Chen, T.; Xu, J. *Polym. Int.* **2001**, *50*, 249.
57. Palermo, E. F.; McNeil, A. J. *Macromolecules* **2012**, *45*, 5948.
58. Liu, R. Y. F.; Hu, Y. S.; Hibbs, M. R.; Collard, D. M.; Schiraldi, D. A.; Hiltner, A.; Baer, E. *J. Polym. Sci. B Polym. Phys.* **2003**, *41*, 289.
59. Kenney, J. F. *Polym. Eng. Sci.* **1968**, *8*, 216.
60. Tharmapuram, S.; Jabarin, S. *Adv. Polym. Technol.* **2003**, *22*, 137.
61. Yuji, A.; Li, L.; Amari, T.; Nishimura, K.; Arashiro, Y. *Macromolecules* **1999**, *32*, 1923.
62. Ihm, D. W.; Park, S. Y.; Chang, C. G.; Kim, Y. S.; Lee, H. K. *J. Polym. Sci.* **1996**, *34*, 2841.
63. Guo, M.; Brittain, W. J. *Macromolecules* **1998**, *31*, 7166.
64. Yu, S.; Saleh A. J. *J. Appl. Polym. Sci.* **2001**, *81*, 11.