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Tailoring block-copolyesters by reactive blending of polyethylene terephthalate and polyethylene naphthalate using statistical design of experiments

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ABSTRACT: Block-copolyesters of polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) were synthesized *via* reactive extrusion. The influence of processing parameters on the material properties on a molecular scale like degree of trans-esterification, block length, and degree of randomness were investigated. The varied process factors were extrusion temperature and rotational speed. The effects of process parameter variation were investigated by ^{1}H-NMR-spectroscopy. The experimental results show a clear dependence of the molecular properties on the processing conditions. By using statistical experimental design (DoE), it was possible to prepare defined copolyesters from PET and PEN without addition of further chemicals. With a degree of randomness between 0.05 and 0.5, the presence of an actual copolyester was confirmed when appropriate extrusion conditions were applied. The reactive extrusion process was confirmed to be suitable to produce defined block-copolyesters in a predictable and reproducible way. It was possible to produce designed sequence lengths, which could be adjusted within a range of 11–136 repeating units in the case of PET and, in the case of PEN, of 2.5–26. The produced materials can be used as barrier materials or barrier coatings to protect substrates against molecular oxygen and water vapour, e.g., in organic photovoltaic applications or food packaging. The described method is a one-pot alternative method to the previously described chemical recycling pathway. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41997.

INTRODUCTION

Long lasting organic materials with good barrier properties against diffusion of small molecules such as molecular oxygen, water, or other volatile compounds are increasingly gaining in significance, especially for packaging applications for organic electronics (photovoltaic cells, etc.). State of the art organic semiconductor molecules such as poly-3-hexylthiophene (P3HT) are typically sensitive against oxidative degradation[1] and therefore need to be embedded in suitable protective materials. Barrier-films consist mainly of stacks of different polymer films or coated organic/inorganic hybrids.[2] Because of their tendency to delaminate, single-phase films might be a suitable alternative. It is well documented that copolyesters of polyethylene terephthalate (PET) with minor amounts of polyethylene

naphthalate (PEN) show improved mechanical[3] and barrier properties.[4] Hence, they are commonly used for encapsulating or protective coating applications and films based on PET/PEN with high barrier qualities (e.g., against water or oxygen) are of great industrial interest. PEN is also described, because of its transparency, to be suitable as a substrate for depositing inorganic substances[5] in low temperature photovoltaic applications.

Many studies related to PET/PEN materials focus on the material itself and its mechanical properties. For instance, Jun *et al.*[6] investigated the crystallisation behavior and discovered that a critical minimum block length is needed for the material to crystallise. Bedia *et al.*[3] studied the mechanical properties of short time melt blended copolyesters of PET and PEN and found that the stiffness of a PEN film can be reduced by adding
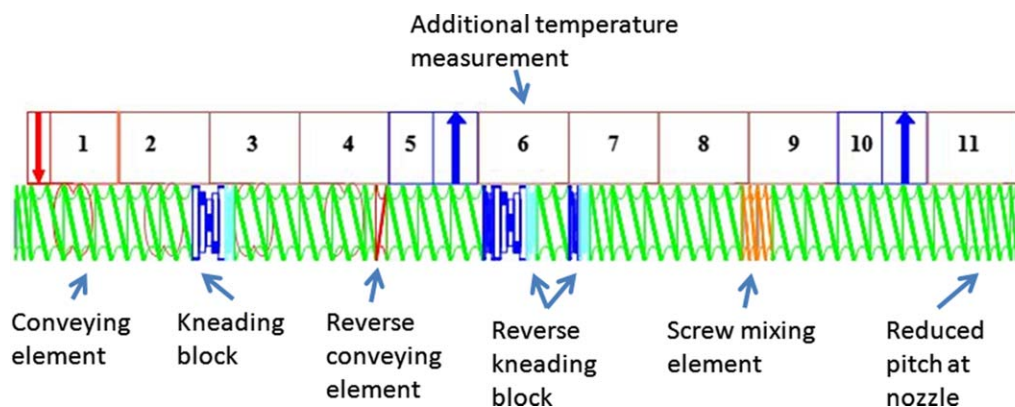
Figure 1. Screw configuration used for trans-esterification *via* reactive extrusion. The main feed is located in the first block (1), whereas blocks 5 and 10 were used for atmospheric (5) and vacuum-degassing (10). The nozzle is located behind Block 11. The additional temperature measurement was performed at the upper surface of the housing block 6. Reaction temperature for trans-esterification was set between block 2 and 11. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a small amount of PET. Yoshioka *et al.*[7] noted a changing morphology by varying the composition. Patcheak and Jabarin[8] investigated the reaction kinetics of trans-esterification and found a second-order kinetic behavior of the direct ester–ester exchange. The influence of the degree of trans-esterification (DT) on the rheological parameters was also described.[9] The work of Yang *et al.*[10] confirmed that and, moreover, found that the second-order kinetics also applied to systems where chain extenders were used to increase the molecular weight. An interesting synthetic method was described that takes advantage of the fact that under the influence of ultrasonic treatment at low amplitudes the trans-esterification reaction is accelerated.[11] In short, much is known and described regarding PET-PEN-copolyester materials, their properties, and even the reaction kinetics of chemical synthesis and modification. However, there is a significant lack of information on the processing of PET/PEN, especially the influence of process parameters on the material performance during the reactive blending of the parent polymer compounds.

Only recently, the tailoring of PET and PEN oligomers for the preparation of PET-PEN-copolyesters comprising blocks of defined block lengths was described.[12,13] Both commercial PET and PEN polymers were first chemically degraded to defined oligomer fragments that were subsequently re-polymerized to give block-copolyesters of defined constitution and tailored properties. In the case of the PET parent polymer, used PET waste material could be used for the process (chemical recycling).[13] However, it would still be beneficial if the design of the block-copolyesters could be achieved without such an additional chemical pretreatment step. Hence, in the current study, an attempt is made to achieve this goal by directly reacting the parent polymers in a controlled way during reactive extrusion.

In the present contribution, a systematic approach is used that illustrates how copolyesters of PET and PEN can be successfully designed with respect to the chemical constitution required for a specific application. This approach is of general interest because in principle it may be transferred to the reactive extrusion of arbitrary block-copolymers. In this article, the manufacturing of trans-esterified copolyesters of PET and PEN containing 20 wt %

of PEN is described. This level of PEN concentration was chosen to obtain a low melt viscosity to guarantee good processability and homogeneous mixing of both polyester components.[14–16] The synthesis was made without addition of further chemicals by reactive blending. The effects of rotational speed and constant homogeneous processing temperature on the material properties on a molecular scale were investigated.

EXPERIMENTAL

Chemicals

Polyethylene terephthalate (PET) with an average molecular weight of 75,533 g/mol was purchased from DSM Unlimited (Sittard, The Netherlands). Polyethylene naphthalate (PEN, Kaladex[TM]) with a density of 1,36 g/mL was purchased from Goodfellow GmbH (Bad Nauheim, Germany). Before processing in reactive extrusion, the commercially available polymers were dried at 120°C for 5 h in a pellet drier. The pellets were stored at 70°C until further processing. The dosage apparatus was held hermetically closed to conserve the dry state. This was done to prevent uncontrolled side effects like hydrolysis. The educts were gravimetrically dosed into the process. The concentration of PEN was kept constant at 20 wt % when copolymerization was brought about in the DoE with a twin-screw extruder.

Determination of Melt Viscosities of PET–PEN Compositions Containing Different PEN Concentrations

Melt viscosities of PET–PEN blends, containing 20, 40, 60, and 80 wt % of PEN (PET80%PEN20%, PET60%PEN40%, PET40%PEN60%, PET20%PEN80%), were measured with a Haake rheometer Rheostress RS 150 (Thermo Fisher Scientific GmbH, Ulm, Germany) equipped with cone and plate. The cone angle was 1°. Melt viscosities were determined at 270°C within a range of frequencies between 0.1 and 100 rad/s.

Preparation of PET-PEN Block-Copolyesters by Twin Screw Extrusion

The synthesis of defined block-copolyesters comprising PET and PEN was performed with reactive extrusion. Therefore, a ZSK25 with L/D 40 twin-screw extruder from Coperion GmbH (Stuttgart, Germany) was used. The screw configuration is illustrated in Figure 1 and was the same for all samples prepared. The
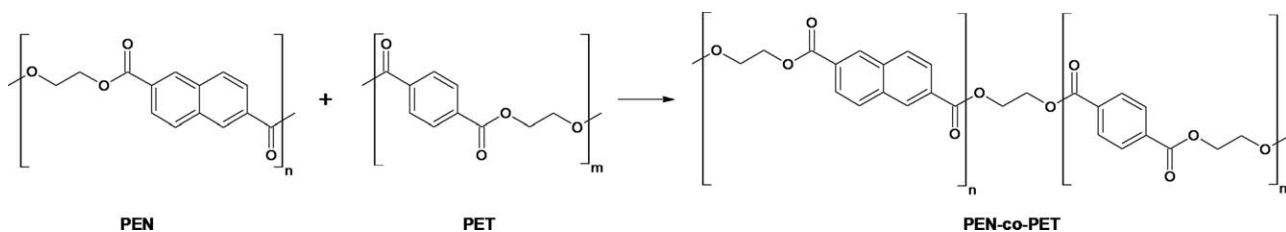
Figure 2. Trans-esterification of PET and PEN polyesters to a copolyester.

dosage of all sample compositions was made in the main feed of the extruder barrel (Figure 1, block 1) at a feeding rate of 4 kg/h.

In the course of reactive blending, the trans-esterification between PET and PEN takes place and ultimately a random-copolyester is formed. The general reaction scheme is shown in Figure 2.

The energy introduced into the system during extruding the material was calculated and correlated to the experimental findings. The specific energy input was calculated as the relationship of engine power P (kW/h) and throughput G (kg/h) in correspondence to the energy that must be provided to produce a specific mass of product (Coperion GmbH).

After the nozzle outlet the polymer melt was immediately cooled to room temperature in a water bath to stop the reaction. To investigate the influence of variations in the processing parameters on the molecular structure and the properties of the resultant block-copolyesters, the processing factors "screw rotational speed" and "extrusion temperature" were changed systematically according to an augmented central composite experimental design that allowed calculating response surfaces *via* linear regression. The rotational speed was varied from 50 to 675 rpm and the pre-set process temperature was varied from 270 to 320°C. Because trans-esterification kinetics are temperature dependent,[14] process temperature was held constant at the chosen levels for the full housing of the extruder (segments 2–11, Figure 1). This was done to guarantee a homogeneous melt[17,18] and to enable quantitative modelling of the resulting material properties on a molecular scale. The temperature of the housing block 1 was held constant at 200°C for all experiments because of technical reasons. The actual temperature at the upper surface of the housing block at segment 6 was measured at all different rotational speeds using an infrared thermal sensor to test the agreement of the set temperature levels with the actual temperatures. No significant deviations were found except for the experiments at high rotational speeds (at 550 and 675 rpm) where slightly higher temperatures than set were systematically found, the deviations being in the range of 4.0–6.8%). Obviously, the cooling capacity of the extruder is not sufficient to keep the block temperature constant and the melt temperatures within the shear zones must be assumed to be even higher at such high rotational speeds.

Experimental Design for Extrusion Parameters
A rotatable two-factor three-level factorial design with four additional axial runs was used and further supplemented by two factor settings at low temperature (experiments 16 and 17, Figure 3) to assess the influence of low temperature in more detail. The

experimental error was determined from two replicates of the center-point of the design (Experiments 4, 7, 11). For the analysis of effects, analysis of variance (ANOVA) was calculated using the statistics software Design Expert 7.0 (Stat Ease, Minneapolis) which is optimized for experimental design. The experimental settings used and the experimental space are visualized in Figure 3.

Response surface models[19] were numerically analyzed for all target responses (the degree of trans-esterification, DT; the degree of randomness, DR; and the statistical block length of the resulting copolyesters, LnPET and LnPEN). The statistical significance of the regression models was evaluated using ANOVA. The quality of the regression models for the degree of trans-esterification (DT), the degree of randomness (DR), and the sequence lengths (Ln) was statistically evaluated by calculating the lack of fit, the correlation coefficient (R^2), and the variance inflation factor (VIF). In addition, the specific energy input was calculated to characterize the energy necessary to produce a given amount of sample as a function of the processing parameters.

All data were tested for normal distribution and the original values were subjected to data transformation where necessary (*i.e.,* models for the block lengths). Various residuals plots confirmed homogenous random variance within the data set and excluded unaccounted effects caused by the actual (randomized) run order used on the experimental result.
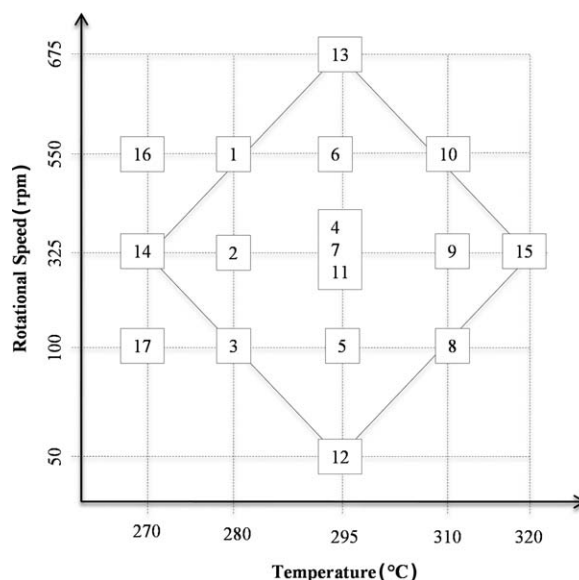

Figure 3. Visualization of the experimental space used in the CCD design. The center-point was compounded three times to estimate the experimental error. Each sample was prepared from PET (80 wt %) and PEN (20 wt %).

To validate the response surface model, a block-copolyester was produced by twin screw extrusion based on experimental settings within the response surface that were not used for establishing the process model. The factor levels for the validation experiment were 300 rpm rotational speed and 300°C reaction temperature.

Structural Characterization of PET–PEN Block-Copolyesters

The block lengths of the block-copolyesters were determined from ^{1}H-NMR spectra similar to a previously described method.[12,13] ^{1}H-NMR spectroscopy was performed at least twice on each copolyester sample using a Bruker AC-250 (Billerica, MA, USA) at 250 MHz. The samples were prepared by milling ca. 20 g of the untreated extrudates to a powder which was subsequently dissolved in $v = 80/20$ deuterated chloroform ($CDCl_3$) and deuterated trifluoroacetic acid ($C_2DF_3O_2$). The chemical shift of an ethylene proton observed in ^{1}H-NMR strongly depends on its chemical environment.

Thus, the proton in an ethylene group that is situated between two naphthalate groups (further abbreviated as H_{NEN} where the index NEN stands for **N**aphthalene-**E**thylene-**N**aphthalene, representing the starting polymer PEN) shows a higher chemical shift at 5.10 ppm (see Figure 4, Table I) than a proton of an ethylene group that is located between two terephthalate groups (chemical shift 5.00 ppm, further abbreviated as H_{TET} where the index TET stands for **T**erephthalate-**E**thylene-**T**erephthalate, representing the other starting polymer PET). Consequently, ethylene protons with two different neighbouring groups (one naphthalate and one terephthalate group, further indexed as H_{NET}) are the result of the trans-esterification reaction and display a chemical shift in between (5.05 ppm). The peak integrals of the different types of protons found in ^{1}H-NMR spectroscopy were used to quantify the varying block composition of PET–PEN-copolyesters in dependence of the processing condi-

Table I. Chemical Shifts of Ethylene Protons

Index	Chemical shift (ppm)	Description
A (H_{TET})	5.00	Ethylene protons, TET
B (H_{NET})	5.05	Ethylene protons, NET
C (H_{NEN})	5.10	Ethylene protons, NEN
D	8.20-8.30	Protons at naphthalate ring
E	8.90	Protons at naphthalate ring
F	8.35	Protons at terephthalate ring
G	8.30	Protons at naphthalate ring

For corresponding NMR spectrum, see Figure 4.

tions. As a characteristic descriptor, the trans-esterification degree (DT) was calculated from the peak integrals (Figure 5, $\int H_{NEN}$, $\int H_{NET}$ and $\int H_{TET}$), using eq. (1)[13]

$$DT = \frac{\int NET}{\int TET + \int NEN + \int NET} \times 100 \quad (1)$$

Based on the peak integrals, the block length (LnPET and LnPEN, respectively) of each segment was calculated using eqs. (2) and (3).

$$P_{NT} = \frac{\int NET}{\int NET + 2 \times \int NEN} = \frac{1}{Ln_{PEN}} \quad (2)$$

$$P_{TN} = \frac{\int NET}{\int NET + 2 \times \int TET} = \frac{1}{Ln_{PET}} \quad (3)$$

where P_{NT} is the probability of finding a terephthalate unit next to a terephthalate unit and P_{TN} is the probability of finding a naphthalate unit next to a terephthalate unit. The sum of P_{NT} and P_{TN} is called the degree of randomness DR. The degree of randomness will change from DR = 0 to DR = 1, if the system
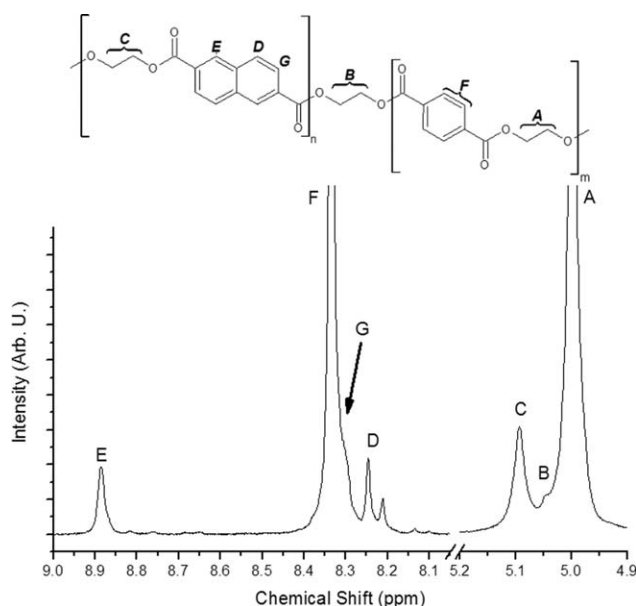

Figure 4. ^{1}H-NMR spectrum of a copolyester that was made from 80 wt % PET and 20 wt % PEN. The Capitals correspond to the nearby signals and are explained in Table I. A graphical classification is given by the simplified structural formula above the spectrum.
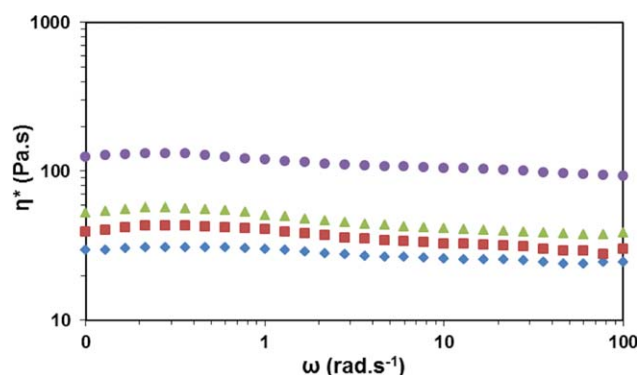

Figure 5. Melt viscosities η^* of different PET–PEN compositions in dependence of frequency (0.1–100 rad/s) measured at 270°C. Blue diamond (◆) PET80%PEN20%, red square (■) PET60%PEN40%, green triangle (▲) PET40%PEN60%, purple circle (●) PET20%PEN80%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

changes from a blend to a random-copolyester.[20] A degree of randomness of DR = 2 is obtained with an alternating copolyester where each terephthalate unit is followed by a naphthalate unit in the polymer backbone.

RESULTS AND DISCUSSION

Influence of PEN Concentration on the Melt Viscosities of PET–PEN Compositions

To study the influence of PEN concentration on the processability of PET–PEN blends, the melt viscosities of a series of PET–PEN blends were determined. It is known from the literature that the melt viscosity of a PET–PEN blend is markedly influenced by the amount of PEN in the mixture.[14] Usually, a minimum in melt viscosity is observed at a certain level of PEN, which is regarded as optimal in terms of processability. However, this optimum varies significantly for the different PET–PEN blends described in the literature and ranges from ca. 10 wt %[14,15] to 40 wt %[16] PEN content. This can be attributed mostly to differences in the molecular weight distribution of the used components which unfortunately, is not always given in the publications. As shown in Figure 5, the melt viscosity in our case was lowest when mixing PET with 20 wt % PEN. Increasing the PEN concentration stepwise up to 80 wt % resulted in an increased melt viscosity of the respective PET–PEN mixture (Figure 5).

A higher melt viscosity not only hampers processability but also results in an increased viscous shearing of the polymer mixture, which in turn leads to local temperature gradients in the melt.[18] Thus, the temperature-dependent trans-esterification rates[14] would non-reproducibly vary throughout the entire melt and thereby increase the experimental error in modelling the influence of the machining parameters on the molecular composition of the extrudate. Hence, the PET–PEN composition with the lowest melt viscosity (PET80%PEN20%) was applied for the experimental design.

Influence of Catalyst on Trans-esterification of PET and PEN

Although the trans-esterification of PET and PEN has been extensively studied by numerous research groups,[21–28] detailed information on the influence of additional chemicals or catalysts on the rate and degree of trans-esterification is only scarcely available from the scientific literature.[29–31]

Ida et al.[30] studied the trans-esterification kinetics of PET–PEN-blends in the presence of different amounts of PET–PEN-block- and PET–PEN-random-copolyesters. The authors expected concentration-dependent effects on the reaction rates and found that the addition of PET–PEN-block-copolyesters increased both the rate and the extent of trans-esterification. Trans-esterification performed in presence of PET–PEN copolyesters leads also to higher degrees of randomness and shorter PET- and PEN-sequence lengths than trans-esterification without addition of PET-PEN-copolymers.[31]

Yang et al.[31,32] studied the influence of the chain extender 2,2′-bis(1,3-oxazoline) (BOZ) on the trans-esterification of PET–PEN-blends. They found that the addition of BOZ increased the trans-esterification via a compatibilizing effect at the interface between the different types of polymeric esters. It is also evident from their study that the BOZ-accelerated trans-esterification yielded a higher degree of randomness in comparison to the un-accelerated reaction.[32]

It should also be expected that trans-esterification of PET and PEN should be strongly enhanced by the addition of catalysts such as metal salts like zinc acetate or other acetates. Such salts have been shown earlier to accelerate both de-esterification[33] and polyester formation[34] reactions. This catalytic effect was confirmed for the zinc acetate/PET–PEN-system in a preliminary experiment, where PET and PEN were processed via reactive extrusion at 270°C in the presence of 1.0% zinc acetate. Addition of this catalyst resulted in a significantly increased trans-esterification degree. The catalysed PET–PEN copolymer also showed a higher degree of randomness (DR = 0.35) than the un-catalysed sample (DR = 0.15).

It is generally accepted that trans-esterification first leads to formation of block copolymer which is then further transformed into random copolymer.[29,32] An increase in degree of randomness could thus be explained by a faster transformation of initially formed block-copolyester due to catalytically active compounds.

The focus of the current study was to evaluate the potential of reactive extrusion to tailor the segment composition and create defined block-copolyesters. Because catalyzed systems seem to favor formation of random block copolymers, in the current study, addition and variation of the amounts of potential catalysts were not considered as factors in the experimental design.

Influence of Reactive Extrusion on Molecular Weight of PET–PEN-Block-Copolyesters

In general, reactive extrusion caused a reduction in molecular weight of the produced copolyesters. The average molecular weights of all copolyester samples measured with GPC were in the range of 30,400–31,600 g/mol and showed polydispersity indices between 2.9 and 3.1. This compares to the molecular weights of starting materials PET (75,533 g/mol) and PEN (47,804 g/mol).

Experimental Design

The influence of extrusion parameters "rotational speed of the extruder screws" (factor 1) and "extrusion temperature" (factor 2) on the molecular composition of the copolyester was studied using a Design of Experiments (DoE) approach.

Extrusion processes of numerous different compounds have been studied earlier using DoE strategies and the same two factors as in our study were always investigated[17,35–41] highlighting the importance of these process parameters. However, although in those studies typically full factorial designs at three factor levels were used, a central composite design (CCD) was used here. The problem dealt with was a response surface problem (optimization problem) and for such a problem CCDs are usually very well suited.[19] A CCD is a two-level factorial design which is supplemented by a center point and circumscribed by so-called star points that are located at a circle containing the factorial. Compared to the three-level factorial approaches usually used, owing to the symmetry of the CCD used here, the two factors were studied at five different levels, which seemed

preferable to us with respect to coverage of the experimental space and accuracy of the model.

Although obviously influences such as the residence time or the pressure build-up during extrusion play an important role as well in extrusion processes, in the current study only the factors "extrusion temperature" and "screw rotational speed" were considered as experimental factors for the following reason. When using a DoE approach, an important pre-requisite for a well-designed experiment is that all studied factors can be adjusted independently and precisely at the selected factor levels, *i.e.,* all studied factors need to be orthogonal. However, orthogonality of factors could not have been achieved when influences like "residence time" or "pressure build-up" would have been included as further factors. For example, by selecting defined levels of extruder screw rotation speed (in rpm) automatically different levels in residence time or pressure build-up would have been obtained. It is not possible to select certain residence times and at the same time independently from that adjust arbitrary levels in rotational speed (without changing the type of extruder machinery used from one experimental setting to the next). Similar problems arise with internal pressure. Although pressure inside the extruder is likely to have an influence on the reaction progress, it is established inside the machinery in dependence of the extruder screw rotation. Hence, it is not possible to explicitly include this influence as an independent factor. In general, influences of that kind cannot directly be addressed as factors in an appropriate DoE study. Nevertheless, of course, it should be kept in mind that these influences should be included in discussing and interpreting the outcome of the DoE.

Extrusion was performed at constant and equal temperature levels for all barrel zones, and some comments should be devoted to this decision as well. Usually, in technical extrusion processes, the temperature settings will be different at different barrel zones to control extruder output rate and quality of the extrudate.[40,42] Hence, from a practical point of view, the systematic variation of heating rates instead of defined and constant temperature levels would at first sight seem to be the appropriate choice of factor. However, Abeykoon *et al.*[18] showed that such variations in barrel zone temperatures cause pronounced temperature inhomogeneities of the melt. Thereby, the resulting model extrudates may not generally be suitable to retrieve representative target response values. Moreover, choosing the "heating rate" as a factor and varying simple temperature gradients until, for instance, a final reaction temperature is obtained, automatically introduces another, aliased factor, the "holding time" at the final temperature. With this, one runs again into the problem of non-orthogonality of the involved experimental factors. At a given level of heating rate, the holding time cannot be varied systematically or kept constant at a certain value unless the length of the extruder (or, the number of barrel zones, respectively) is changed accordingly from one experimental setting in the heating rate to another. The consequence would be that the experimental space covered by the experimental design was highly asymmetrical, *i.e.,* the combination of the high level in heating rate with the high level in holding time is not possible and neither is the combination of low

heating rate with low holding time. The informative value of such an experimental design would be rather low. At least in principle, with different heating rates, the symmetry and equal distribution of the design points over the experimental space could be achieved *via* shortening or extending the extruder. But then again, if different extruder block lengths were used, one would run into the practical problems associated with varying the screw configurations from experiment to experiment. It is likely that additional variation is introduced into the data set thereby increasing the experimental noise and reducing the statistical significance. The situation becomes even more complicated if it is intended to investigate more complex heating profiles.

Therefore, earlier studies focussing on the quantitative modelling of the influence of extrusion parameters on extrudate characteristics like our present study also consistently relied on uniformly set barrel zone temperatures throughout the experimental design.[36–38] This minimizes the induced temperature gradients in the melt ("thermal noise"), provides as homogeneous chemical properties of the extruded products as possible and allows the quantitative correlation of the extrudate properties with defined temperature settings.[18]

Degree of Trans-esterification

Figure 6 shows the ^{1}H-NMR spectra of block-copolyesters obtained at different extrusion temperatures ranging from 270 to 320°C at a fixed rotational speed of 325 rpm to illustrate the influence of the extrusion temperature on the extent of trans-esterification. The changes in chemical shifts and relative
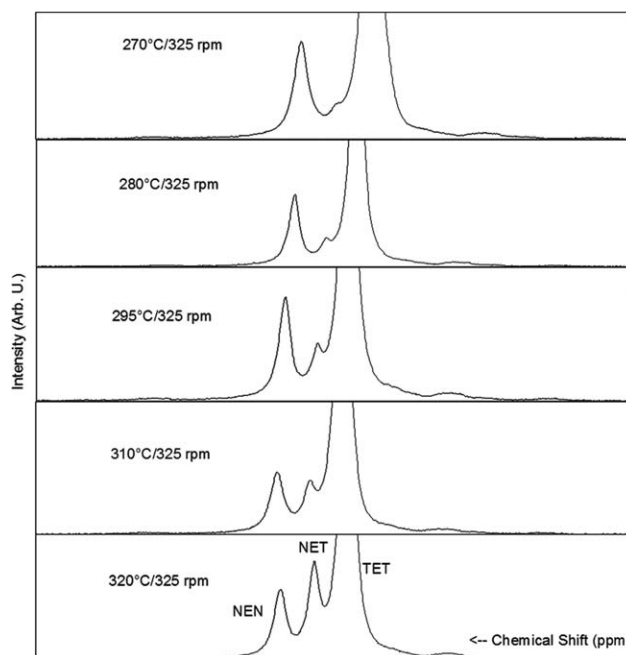

Figure 6. Comparison of the different ^{1}H-NMR resonance peaks. TET means two neighboring terephthalate units, NEN, respectively, two neighboring naphthalate units. This both peaks also can be found from the virgin educt polyesters PET and PEN. The peak in the middle corresponds to the ethylene protons that now have two different neighbors. In the case of a physical blend, this peak will disappear.

intensities of the different types of ethylene protons in dependence of the reaction temperature are clearly seen.

The signal intensity of the H_{NET}-peak is indicative for the extent of conversion into block-copolyester that has taken place and is strongly influenced by the extrusion temperature. Under increasingly harsh reaction conditions at higher temperature, this peak increases and corroborates the actual formation of a block-copolyester. On the other hand, mild reaction conditions during extrusion (low temperature and low rotational speed) yielded hardly any trans-esterification at all (Figure 6, at 270°C/325 rpm), *i.e.,* under such conditions mostly a physical blend was formed as indicated by the near absence of the interjacent H_{NET} ^{1}H-NMR.

The values for the molecular response factors (*i.e.,* the degree of trans-esterification, DT; the degree of randomness, DR; and the statistical block length of the resulting copolyesters, LnPET and LnPEN) for the complete design of experiments as determined from ^{1}H-NMR measurements are summarized in Table II.

The influence of the process parameters "rotational speed" and "extrusion temperature" on the extent of trans-esterification and the exact chemical composition of block-copolyesters of PET and PEN was studied quantitatively in more detail using ANOVA and response surface methodology. The statistical analysis of the effects of rotational speed and processing temperature on the degree of trans-esterification (DT) is summarized in Table III. Data for both a linear and a quadratic model are given. In addition the statistical analysis of the effects on the statistical block length of PET (LnPET) and PEN (LnPEN) and the degree of randomness (DR) are presented.

The ANOVA results show that for both models the VIF (variance inflation factor) is equal or close to 1. Hence, the distortion of the symmetry of the overall factorial design by the introduction of the additional experiments at low temperature can be neglected. The model equations in actual factors for the two models that determine the shapes of the response surfaces are $DT_{linear} = 41.28 + 0.011^{*}A + 0.156^{*}B$ for the linear model and $DT_{quadratric} = -40.96 - 1.397^{*}10^{-4*}A + 0.159^{*}B + 1.574^{*}10^{-5*}A^2$ for the quadratic model, respectively, where A is the rotational speed and B is the processing temperature. The quadratic model contains only one additional quadratic term in rotational speed. The corresponding response surfaces are depicted in Figure 7(a,b) and show a tilted plane in the case of the linear model [Figure 6(a)] and a slightly twisted plane of similar tilting angle in the case of the quadratic model.

With both models, the influence of the extrusion temperature seems to be clearly linear, whereas the statistical parameters describing the factor "rotational speed" give no such clear indication whether to preferably postulate a linear or rather a quadratic dependence.

The quadratic term in "rotational speed" has a P>F-value of 0.0644, which is >0.05, the statistical limit representing an error of 5%. Hence, at the chosen significance level, it is not statistically significant. Including this term nevertheless in the overall factor equation the quadratic model is found to show a smaller standard deviation and a somewhat lower coefficient of variation (C. V.). The coefficient of correlation (R-Squared) is also slightly closer to 1 in the case of the quadratic model and a smaller probability to have a significant lack of fit to describe

Table II. The Degree of Trans-esterification (DT), Degree of Randomness (DR), the Statistical Block Length of the Two Segments (L_{nPET} or L_{nPEN}) and the Standard Deviation (Err(x)) as Calculated from NMR-Analysis

ID	Rotational speed [rpm]	Temperature [°C]	DT %	DR	Ln_{PET}	Ln_{PEN}	E kWh/kg	Notice
1	550	280	7.18 ± 0.34	0.24 ± 0	22.89 ± 1.26	4.99 ± 0.06	0.2622 ± 0.0149	Design
2	325	280	5.2 ± 0.1	0.19 ± 0	32.08 ± 0.69	6.42 ± 0.06	0.1928 ± 0.0108	Design
3	100	280	4.29 ± 1.34	0.15 ± 0.05	40.85 ± 12.96	8.13 ± 2.36	0.0855 ± 0.0034	Design
4	325	295	7.05 ± 0.21	0.25 ± 0	23.59 ± 0.78	4.77 ± 0.04	0.1646 ± 0.0089	Design
5	100	295	6.00 ± 1.42	0.21 ± 0.04	28.3 ± 7.11	6.02 ± 1.04	0.0663 ± 0.0049	Design
6	550	295	8.34 ± 1.58	0.31 ± 0.04	20.59 ± 4.25	3.85 ± 0.37	0.2557 ± 0.0124	Design
7	325	295	6.86 ± 0.54	0.25 ± 0.02	24.43 ± 1.96	4.81 ± 0.33	0.166 ± 0.0065	Design
8	100	310	7.64 ± 0.78	0.27 ± 0.02	21.88 ± 2.33	4.45 ± 0.35	0.0535 ± 0.0024	Design
9	325	310	9.64 ± 0.65	0.35 ± 0.02	17.33 ± 1.25	3.46 ± 0.15	0.1351 ± 0.0105	Design
10	550	310	12.54 ± 0	0.42 ± 0.01	13 ± 0.07	2.95 ± 0.07	0.2156 ± 0.0119	Design
11	325	295	9.6 ± 0.06	0.3 ± 0	16.64 ± 0.09	4.2 ± 0.04	0.1888 ± 0.012	Design
12	50	295	6.09 ± 0.46	0.19 ± 0.01	26.2 ± 2.01	6.76 ± 0.46	0.0491 ± 0.0034	Star
13	675	295	14.74 ± 0.35	0.49 ± 0.01	11.08 ± 0.27	2.49 ± 0.05	0.3439 ± 0.007	Star
14	325	270	4.41 ± 0.23	0.15 ± 0.01	37.23 ± 2.08	8.2 ± 0.33	0.2729 ± 0.0049	Star
15	325	320	12.44 ± 2.69	0.45 ± 0.04	13.82 ± 3.4	2.64 ± 0.16	0.1551 ± 0.0059	Star
16	550	270	6.78 ± 0.34	0.25 ± 0.01	24.65 ± 1.31	4.88 ± 0.18	0.139 ± 0.0043	Additional
17	100	270	1.31 ± 0.46	0.05 ± 0.02	136.6 ± 48.25	26.64 ± 9.37	0.401 ± 0.02	Additional

Table III. Statistical Evaluation Data from the ANOVA for the Models of the Degree of Trans-esterification (DT), Block Lengths of PET and PEN (LnPET, LnPEN), and the Degree of Randomness in Dependence of the Rotational Speed During Reactive Extrusion

	DT^a $P>F$	DT^b $P>F$	$LnPET^a$ $P>F$	$LnPEN^a$ $P>F$	DR^a $P>F$
Model	<0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
A^c	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
B^d	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
A^{2e}	n.a.	0.0644	n.a.	n.a.	n.a.
Lack of fit	0.4656	0.5361	0.4170	0.1570	0.2490
Std. Dev.	1.1879	1.0754	0.0182	0.0318	0.0351
C.V. %	15.5205	14.0505	8.7182	6.9812	13.2273
PRESS	31.1581	34.8175	0.0075	0.0242	0.0281
R-Squared	0.8889	0.9155	0.8845	0.9241	0.9177
Adj R-Squared	0.8731	0.8960	0.8680	0.9133	0.9059
Pred R-Squared	0.8248	0.8043	0.8121	0.8699	0.8658
Adeq Precision	22.0333	20.9086	21.5447	27.1766	25.9969

[a] Statistical evaluation using a linear model.
[b] Statistical evaluation using a quadratic model.
[c] A: effect of rotational speed
[d] B: effect of temperature
[e] A^2 quadratic effect of rotational speed;

the data is also found. The adequate precision is the predicted response relative to its associated error (signal/noise-ratio) and is in both models relatively similar. The predicted residual sum of squares (PRESS) value suggests a slightly worse fit with the quadratic model.

From Figure 7(a,b), it is evident that at low reaction temperatures and low values for the rotational speed trans-esterification will occur only to a limited extent or not all. However, in contrast to the linear model, the quadratic model suggests nonlinear behavior of the trans-esterification degree. Such nonlinearity is plausible when considering a shear induced increase in the actual melting temperature as the rotational speed increases.

The actual temperature of the melt can be safely assumed to be always higher than the temperature of the surrounding machining parts due to shear heating and this deviation might become evident as the non-linearity described by the quadratic model. The shear heating effect is also seen in the slight deviations of the housing temperature at the mixing zone (Figure 1) from the pre-set extruder temperatures at rotational speeds >550 rpm.

Moreover, the energy input also increases with increasing rotational speed which in turn should yield higher trans-esterification degrees (Figure 8). However, a further increase in temperature tends to decrease the mechanical energy input again because the melt viscosity decreases at higher
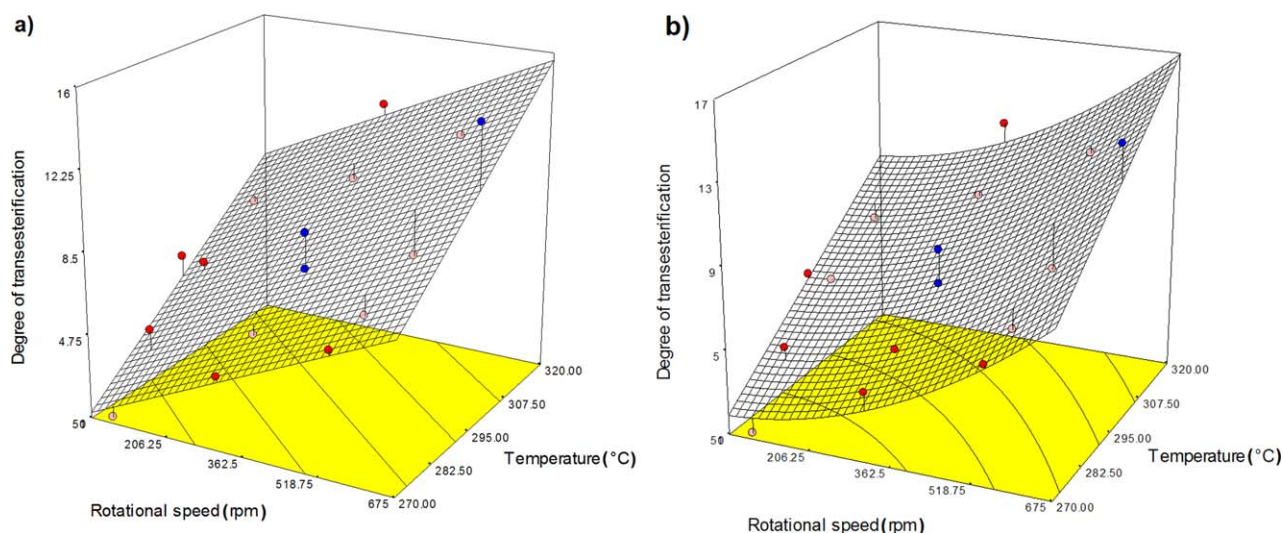

Figure 7. Model graphs of the degree of trans-esterification in dependence of the process parameters "rotational speed" and "extrusion temperature". (a) linear model; (b) quadratic model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
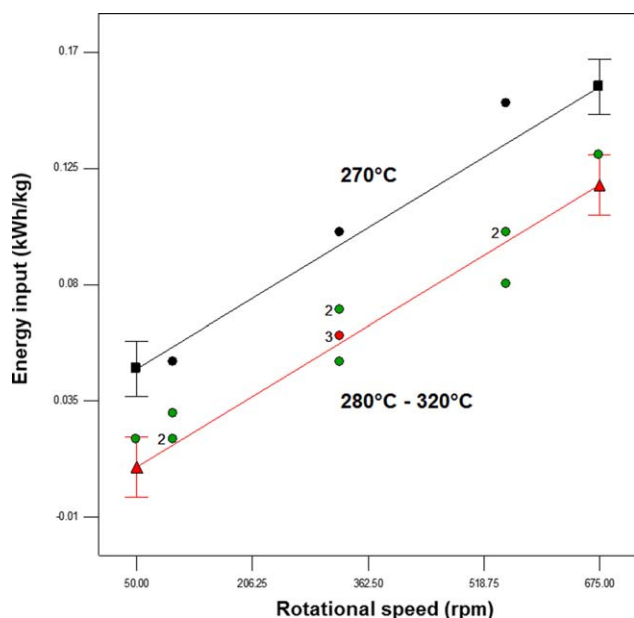
Figure 8. Energy input at different process temperatures. Upper black line shows the energy input at low temperature (270°C), the lower red line at higher temperatures (280–320°C), as a function of rotational speed. Values are taken from internal process sensors and averaged over 5 min with a resolution of 20 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperatures. Hence, the overall observed effect of rotational speed appears to be nonlinear, and it is therefore, assumed that the quadratic model [visualized in Figure 7(b)] obtained for the trans-esterification degree in dependence of the extrusion conditions should provide a more realistic view of the system.

Sequence Length

The response surfaces for the dependence of the sequence lengths of the prepared copolyesters on the varied process parameters are summarized in Figure 9(a) (for the PET block

lengths, LnPET) and Figure 9(b) (for the PEN block lengths, LnPEN). By expressing the measured values for the block lengths as the reciprocal of their square roots, the decrease of both LnPET and LnPEN with increasing rotational speeds and processing temperatures can be displayed in a linear form. It should be noted that at low temperatures and low rotational speeds the highest block lengths [*i.e.,* the smallest values in Figure 9(a,b) due to the transformed ordinate] were observed.

The ANOVA for the block length is given in Table III. The coefficient of variation (C. V.) was 7.0% in the case of LnPEN and 8.7% for LnPET in the transformed scale. There was no significant lack of fit across the design space and the coefficients of correlation were acceptably high. Because both adjusted and predicted R^2 are similar and close to one, the predictive power of the model is satisfactory. From the values for the adequate precision, it can be deduced that the probability for the found effects being caused by noise is low.

The absolute statistical length of one repeating unit within a polymer chain can be taken from Table I. By appropriately varying the process parameters, the block length can be driven to take on values between about 11 and 136 repeating units in the case of PET. The sequence length of PEN—because of the smaller mass fraction of only 20%—can be arbitrarily adjusted between 2.5 and 26.5 repeating units. According to the response surface model, the overall dependence of each block length on the varied process parameters can be described by eqs. (4) and (5). However, the resulting block lengths cannot be arbitrarily adjusted separately. Extrusion conditions that lead to extensive de-polymerization of PET always lead to high degrees of de-polymerization in PEN because both components are coextruded. In turn, no block-copolyesters can be designed comprising of small block lengths in PEN and at the same time large block lengths in PET. A linear relationship between the block lengths of PET and PEN in the resulting block-copolyesters was obtained (Figure 10). Hence, with respect to the tailored design of the block-copolyesters, it must be considered that once a
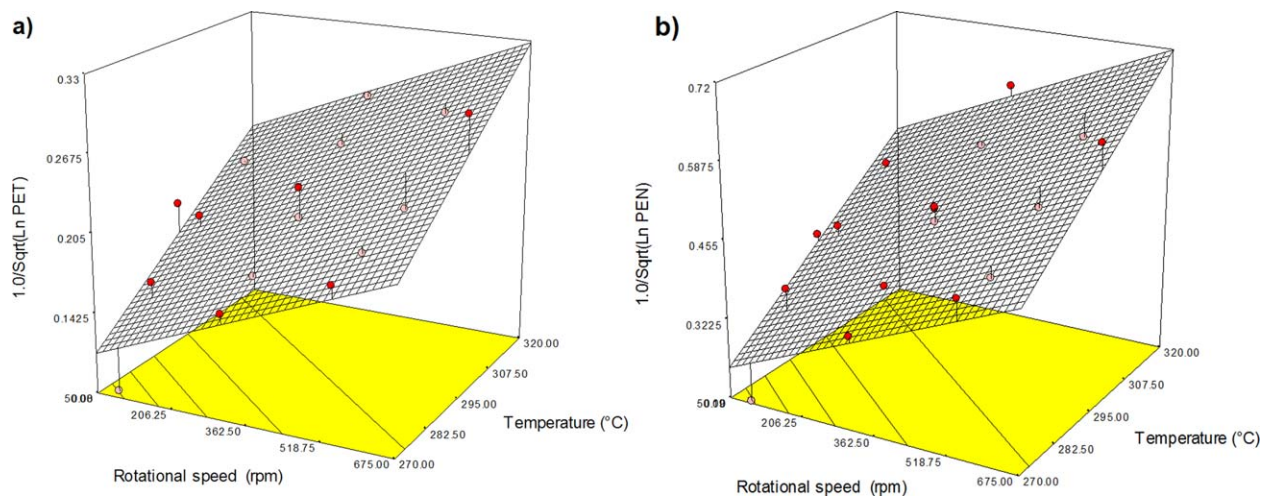

Figure 9. Model graphs of the sequence length of PET (a) and PEN (b) in dependence of the process parameters "rotational speed" and "extrusion temperature". The values were calculated from ^{1}H-NMR-data and averaged from a double determination. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
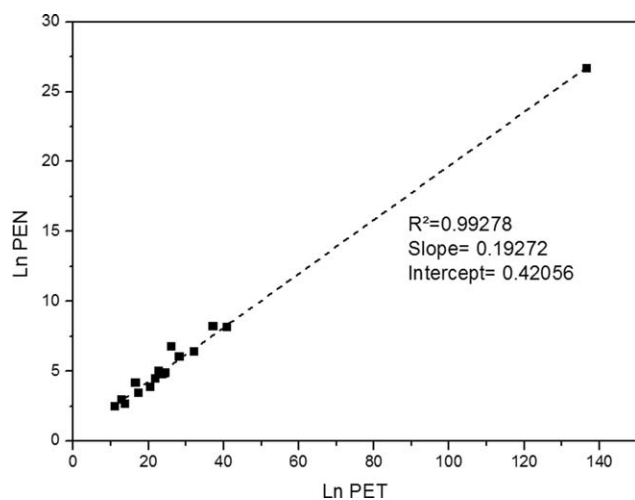
Figure 10. Scatter plot of the determined block length of both segments from all design-samples.

targeted PET sequence length is realized by appropriate process conditions as suggested by the response surface model, a corresponding PEN sequence length is automatically obtained.

$$(\mathrm{LnPET})^{-1/2} = -0.529 + 1.572 \times 10^{-4} \times A + 2.347 \times 10^{-3} \times B \quad (4)$$

$$(\mathrm{LnPEN})^{-1/2} = -1.171 + 3.455 \times 10^{-4} \times A + 5.18 \times 10^{-3} \times B \quad (5)$$

Degree of Randomness

The effect of temperature and rotational speed on the degree of randomness is illustrated by the response surface diagram given in Figure 11. A direct proportionality between the degree of randomness and the factor settings was obtained. Thus, with increasing temperature and increasing rotational speed, the extrudate changes from a physical blend into a copolymer.

Low rotational speed means that the residence time of the liquefied material in the extruder is longer. However, as a result of the lower
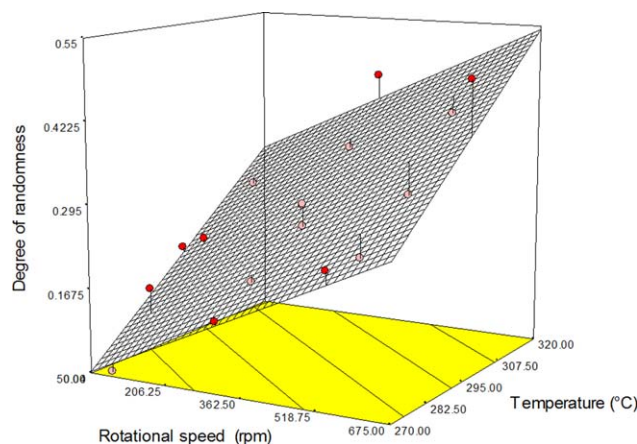

Figure 11. Model graph of the degree of randomness in dependence of the process parameters "rotational speed" and "extrusion temperature". [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Validation Result of the Quadratic Response Surface Model Describing the Reactive Extrusion of PET/PEN Trans-esterification

Response	Prediction	Validation	PI high	PI low
DT [%]	8.07	6.79	2.47	2.47
Ln PET	20.17	24.25	9.97	5.73
Ln PEN	4.23	5.21	1.56	1.01
DR	0.30	0.23	0.08	0.08

The prediction interval (PI) contains a significance of 95%.

screw speed the mixing performance is suboptimal compared to the case of higher rotational speed. Although with a higher rotational speed the residence time is shorter the mixing is more intense. Mixing performance is generally considered more important than residence time for achieving a homogeneous (alternating) polymer with a very small sequence length. The model equation derived from linear regression is given by Equation 6:

$$DR = -1.45 + 3.665 \times 10^{-4} \times A + 5.459 \times 10^{-3} \times B \quad (6)$$

The corresponding ANOVA is summarized in Table II. The model shows a typical experimental error in terms of coefficient of variation (C. V.) of 13.23%. The coefficients of correlation are quite similar and the adequate precision is sufficiently high. It is not possible to produce alternating copolyesters (DR > 1) with the given extruder settings within the used process window. From an analysis of data in Table II it may be concluded that the block length of PEN can be reduced to about 2.5. This means that only one to two more steps of the reaction must take place to create isolated repeating units of PEN. Because an increasing mixing efficiency leads to higher conversions, it should be possible to produce random-copolyesters with a more aggressive screw configuration. In Figure 1, it is shown that in the current extrusion layout, the region from block 7 to block 11 is only equipped with conveying elements and therefore blocks 7 to 11 do not contribute any mixing power to the process. Hence, if in this region further kneading units would be integrated in a conveying or anti-conveying configuration, the mixing power of the overall system could be significantly increased[43] to allow a further increased conversion.

For validation, a block-copolyester was produced using experimental settings within the response surface that were not used for establishing the process model. The parameters were 300 rpm and 300°C. The results are shown in Table IV. The validation indicates that all molecular markers can be predicted from the developed models with sufficient precision.

CONCLUSIONS

Reactive blending of polyethylene terephthalate and polyethylene naphthalate was performed under systematic variation of the main process variables extrusion temperature and rotational speed with the aim to prepare copolyesters of tailored block sequence. The experiments show that the molecular structure of the processed copolyesters can be controlled by varying the processing parameters. To describe the process of trans-esterification in a reactive extrusion the process was modelled using response surface methodology. Response surface models

were developed for the degree of trans-esterification, the degree of randomness and the block length. It was observed that the conversion increases with increasing temperature and rotational speed. Because of shear heating, a quadratic model was preferred to describe the effect of rotational speed. Based on this model, it is not sufficient to raise the temperature at a low rotational speed to achieve a high conversion. Hence, mixing efficiency is more important than temperature to reach high conversions. The combined effect of increasing temperature and rotational speed results in a further increase in conversion. All models had satisfying R^2 values. It is concluded that reactive extrusion is an appropriate method to produce defined copolyesters in a continuous way and the molecular characteristics can be adjusted by varying the processing parameters. This helps to prevent problems, caused by discontinuous methods, e.g., first batch effect. The given block-copolyesters comprising PET and PEN can be used in barrier applications, for example, food packaging or as barrier films in an organic electronic use. The formation of a block-copolyester (PET-co-PEN) is possible with the given and standardized extruder settings and without further catalysts. This prevents possible problems that might be caused by addition of chemicals.

Although this study dealt with catalyst-free raw material formulations, the quantification of the effect of adding catalysts such as zinc chloride or others on segment composition in reactive extrusion still requires experimental investigation. It would be expected that trans-esterification should yield random copolymers rather than block copolymers under otherwise same processing conditions because catalysts have been shown to accelerate both de-esterification and polyester formation, thereby leading to higher degrees of trans-esterification and randomness and correspondingly smaller sizes of the resulting PET and PEN segments.

ACKNOWLEDGMENTS

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