

# Synthesis and Characterization of Star-Branched PA12 Grafted Onto PEi Core Molecule

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**ABSTRACT:** Synthesis of PEi-g-PA12 with concentration of PEi 2–40 wt % was fulfilled in two different ways, as ring-opening polymerization of LL and transamidation of linear PA12 in the presence of core PEi molecules. Both methods provide almost uniform materials. Obtained samples were characterized using different techniques: solution and melt viscosity, molecular weight and molecular weight distribution of star polymers and PA12 “arms” with different content of cores, as well as melt and glass transition measurements, were fulfilled. For clarification of PEi-g-PA12 structure and mechanism of grafting, bis- (hexameth-

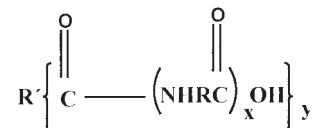
ylene)triamin and tris(2-aminoethyl)amin were used as a model core molecules. Participation of not only the primary but also the secondary and tertiary amino groups in the formation of PEi-g-PA12 polymers (until 2–8 wt % of PEi content) have been established. At higher content of PEi (8–15 wt %), only primary amino groups of core molecules take part in grafting. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2413–2422, 2005

**Key words:** star polymers; branched; polyamides; polyimines; transamidation

## INTRODUCTION

Star-branched polymers have been known a long time. Paul J. Flory, in the early 1950s,<sup>1</sup> provided a method of preparation of thermoplastic macromolecular polymers with branched structure. Before that it was known, according to works of W. H. Carothers,<sup>12</sup> that only two types of condensation linear polymers, obtained by condensation of bifunctional monomers, have thermoplastic properties. All previous attempts to add some amount of polyfunctional reactant to condensing monomers caused the formation of thermoset, or gelled, products in place of the thermoplastic polymers that would otherwise be formed. However, in the present time, hyperbranched polymers, possessing thermoplastic characteristics, have been made using a combination of polyfunctional monomers.<sup>2</sup> In this work, gelation can be avoided by selecting the extent of reaction ( $p$ ), the ratio of reactive groups ( $r$ ), and the number of functional groups per each type of monomer molecules ( $x$  and  $y$ ) so that the relation  $rp^2 \leq 1/[(x-1)(y-1)]$  is satisfied. In spite of existed in that time teaching Flory<sup>13</sup> proposed a method of preparation of new polyamides from polybasic acids having six or more carboxylic acid groups, or their derivatives, such as esters, amides, acid chlorides, or anhydrides, by condensation with amino ac-

ids, having only one amino group and one carboxylic group, or derivatives of these acids (esters, amides, lactams).<sup>1</sup> New polyamides were not linear and therefore did not possess a network structure. Their structure can be represented by the formula:



where  $R'$  is the nucleus of the polybasic acid having six or more carboxylic acid groups, and  $y$  represents the number of chains.

Flory showed a possibility of variation of the arms' length and their amount by changing of molar ratio of bifunctional monomers and polyfunctional cores and, as a result, differentiation in the properties of new polymers. He also pointed out application approaches of these polymers. Short chain polyamides, and those having few chains, he supposed to be useful as coating compositions or adhesives or for preparation of molded objects. The higher molecular weight compositions are frequently crystalline in nature and can be drawn into strong elastic fibers.

Since that time, star-branched polymers have been actively studied. In general they are regarded as multi-chain polymers, in which a number of polymer chains or “arms” extend from a branch point (core).

They are not limited by class of polycondensed polymers. Preparation procedure can involve anionic and cationic as well as condensation mechanisms.

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Thus, for example, star- branched polystyrene was prepared by the linking of living anionic polystyrene with silicon tetrachloride.<sup>3</sup> As another example, grafting of living cationic poly(tetrahydrofuran) onto amino dendrimers can be given.<sup>4</sup>

As a core molecule, large scale polyfunctional ( $f \geq 3$ ) agents, including low molecular weight compounds, as well as polymers or dendrimers, can be used.

There are several techniques for star-branched polymer preparation. They are: coupling of already existing polymers with functional end groups with end groups of a core (without chain breaking reactions),<sup>4</sup> termination (or initiation) of the polymerization process of a corresponding monomer by core molecules, or reactions of redistribution of polymer chains caused by functional end groups of cores (e.g., transamidation, transesterification).

Dendrimer structures as a core for star-shaped polymers allow obtaining samples of definite structure and low MWD, but are not appropriate for industrial scale. An example of star polyesters and polyamides forming from dendrimer cores is star-branched polycaprolactones, obtained from polypropylenimine dendrimers and caprolactone or polycaprolactone and polycaprolactam.<sup>5</sup>

J. M. Warakowski has described<sup>6</sup> the preparation of star-branched poly( $\epsilon$ -caprolactam) based on polyethylene imines of different generation as a core and initiator for the ring-opening polymerization of  $\epsilon$ -caprolactam. There are also mentioned two other methods of poly( $\epsilon$ - caprolactam) preparation: (1) starting from a core molecule with several carboxy acid sites, on which a star-branched polymer is formed by means of ring-opening polymerization, and, (2) from tris caprolactam as a core molecule and anionic polymerization of  $\epsilon$ - caprolactam.

Borggreve and coworkers patented a method of synthesis of star-branched polymers by reaction in melt from a polymer having at least one hetero-atom in the chain with a compound having at least three functional groups.<sup>7</sup> Examples of such polymers are polyamides, polyurethanes, polyesters, polyoxyalkylenes, polyimides, and copolymers of these. In the case of polyamides, preference was given to dendrimer amines as core molecules. The authors prepared a star-branched nylon 6 from a mixture of this polymer and 1,4-diaminobutane-*N,N'*- tetra-1-propylamine when extruding at 270°C with a retention time of 3 minutes.

Oenbrink and colleagues provide a method for preparation of polyamide graft copolymers containing graft chains derived from a combination of diamine and dicarboxylic acid using polyamine cores. Haeger and colleagues prepared highly branched polyamide graft copolymers by grafting of lactams or  $\omega$ -carboxylic acids onto polyamine core molecules in the presence of a small amount of di- or tricarboxylic acid.<sup>9</sup>

These copolymers were claimed to possess a high solvent resistance.

In order to examine in detail some important properties of polyamine grafted highly branched polyamide copolymers with different degrees of branching, star-branched PA12 grafted onto a PEi core (PEi-g-PA12) was prepared by ring-opening polymerization of LL and transamidation of linear PA12 in the presence of PEi according Haeger et al.<sup>9</sup>

## EXPERIMENTAL

### Materials

LL and linear PA12 ( $\eta_{rel} = 1,6$ ;  $[-COOH] = 72$  mmol/kg,  $[-NH_2] = 68$  mmol/kg) were available from Degussa AG. PEi (Lupasol G 100, poly-ethylenimine from BASF AG, Ludwigshafen, Germany, 50% aqua solution,  $M_w = 5000$ ); phthalic acid, 99.5% (Fluka); tris(2-aminoethyl)amine, 96% (ACROS Organics); bis(hexamethyl)triamine, 93.39% (Du Pont); and *N*-methyl-2-pyrrolidone (NMP), 99.5% (Merck) were used directly.

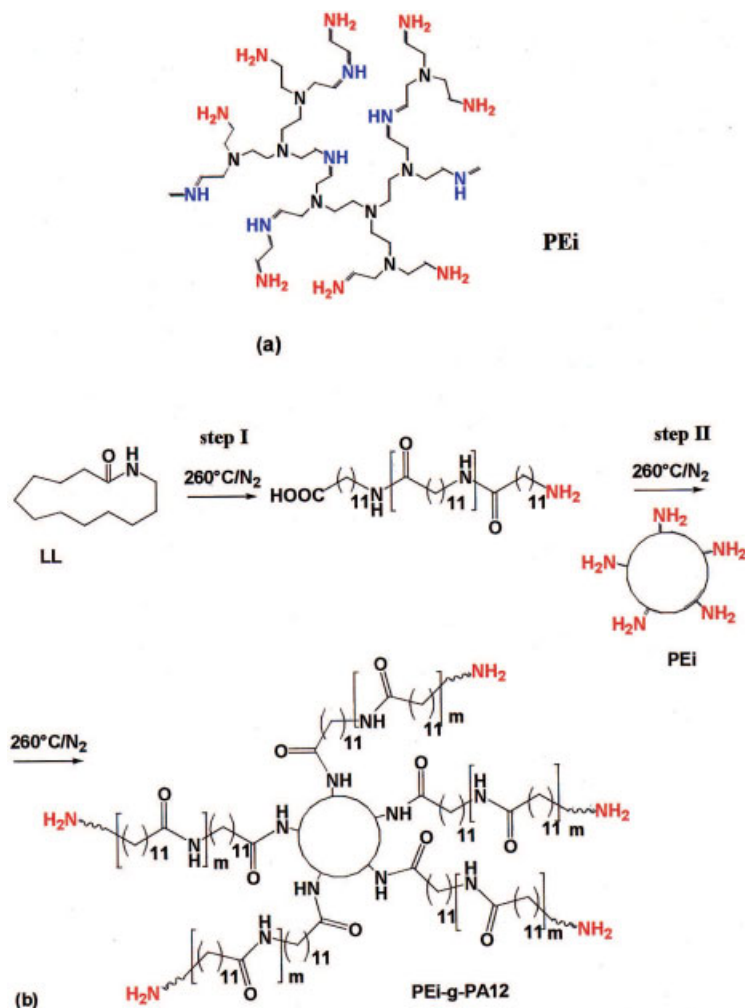
### Method 1: synthesis of star-branched polyamide 12 from LL (Scheme 1, steps I and II)

LL (8 kg) was melted and transferred into a pressure-tight polycondensation vessel, where 500 ml of water and 10–200 ppm of catalyst were added. The cleavage of LL was conducted at 290°C under autogenic pressure during 6 hours (Scheme 1, step 1). Pressure was then slowly reduced to 10 bars, and temperature decreased to 265°C (step II). PEi (50% aqua solution) was added in amounts of 2–10 wt % (calculated for pure PEi) according to LL. After 30 min stirring pressure was reduced to 1 bar and the reaction was conducted for 4 hours. Melt was discharged in the form of an extrudate, cooled and palletized.

### Method 2: Synthesis of star-branched polyamide 12 from linear polylauro lactam (Scheme 1, step II)

At a laboratory scale 100 g of linear polylauro lactam was melted and PEi (50% aqua solution) was added in amounts of 2–40 wt % (calculated for pure PEi). Stirring was continued during 5 hours at 260°C and stream of nitrogen. Melt was discharged, cooled, and cut.

At a bigger scale, 8 kg of granulated linear polylauro lactam ( $M_n = 15,000$ ) was melted and transferred into a pressure-tight polycondensation vessel; PEi (50% aqua solution) was added in amounts of 2–10 wt % (calculated for pure PEi) according to LL at 260°C under a stream of nitrogen. Stirring was continued during 1 hour. After that, pressure was slowly reduced to normal atmospheric, and stirring was con-



**Scheme 1** (a) Polyethylenimine (PEI); (b) synthetic scheme of star-branched polyamide 12 from lauro lactam (step I, II) or polylauro lactam (step II) and multifunctional core molecule (PEI).

tinued for 6 hours with nitrogen flowing over the melt. The melt was discharged in the form of an extrudate, cooled and palletized.

#### Grafting of polyamide 12 onto bis-(hexamethylen)triamin BHMT

Linear PA12 was melted in the presence of different amounts of BHMT under  $260^{\circ}\text{C}/\text{N}_2$  for 4 hours.

#### Grafting of polyamide 12 onto tris(2-aminoethyl)amin TAEA

Linear PA12 was melted in the presence of different amounts of TAEA under  $260^{\circ}\text{C}/\text{N}_2$  for 4 hours.

#### Reaction of polyamide 12 grafted onto bis-(hexamethylen)triamin with phthalic acid PHA

Samples of branched PA12 were brought into contact with PHA, which was taken in excess according to the

amount of amino groups in the branched PA12. The reaction was conducted in melt under  $\text{N}_2$ ,  $T = 260^{\circ}\text{C}$ , 4 hours. Color of melt doesn't change during the reaction. To get rid of the excess of unreacted PHA, samples were purified by extraction (4 h boiling in ethanol) or precipitation from NMP. Amino and carboxylic groups' concentration was determined before and after reaction with PHA and the purification procedure (Table I). IR- spectra of samples were measured after purification (Table II).

#### Reaction of polyamide 12 grafted onto tris(2-aminoethyl)amin with phthalic acid

Conditions of the reaction were the same as in the previous example. Purification procedure and IR-spectroscopic measurements were fulfilled as is described above.

**TABLE I**  
**Amino [amino] and Carboxylic [-COOH] Group Concentration in Samples of PA12 Branched in the Presence of Bis(hexamethylen)triamin BHMT before and after Reaction with Phthalic Acid PHA and after Purification (Extraction and Reprecipitation) on the Results of Titration. [-COOH] before Reaction with PHA for Samples XI–XIV < 5 mmol/kg**

N	BHMT used for PA12 branching, wt %	[amino] <sub>0</sub> before reaction with PHA, mmol/kg	[amino] after reaction with PHA, mmol/kg	[-COOH] after reaction with PHA, mmol/kg	[-COOH] after extraction, mmol/kg	[-COOH] after reprecipitation, mmol/kg
XI	1.3	187	3	23–24	24	20
XII	0.8	171	0	32	27	23
XIII	3.0	339–350	4–5	80	65	57
XIV	5.0	555–558	34	30	—	25

### Differential scanning calorimetry (DSC)

The melting and glass transition behavior of PA12-g-PEi samples were investigated by DSC using a DSC 7 device (Perkin–Elmer) with Pyris Software for Windows. Measurements were carried out in a temperature range from  $-90$  up to  $210^{\circ}\text{C}$  with scanning rate of  $\pm 20\text{K}/\text{min}$  as cycles consisting of 1.heating - cooling - 2.heating scans. The temperature and heat transitions were calibrated with Ga, In, Sn, and Bi standards.

### Determination of carboxylic end groups

0.5 g of graft polymer was dissolved in 50 ml of benzyl alcohol at  $165^{\circ}\text{C}$  under nitrogen during 15 min. The solution was titrated with a solution of KOH (0.05 mol KOH/l) in ethylene glycol using phenolphthaleine as indicator.

### Determination of amino groups

0.2–0.5 g of graft polymer was dissolved in 50 ml of m-cresol at  $25^{\circ}\text{C}$ . The solution was titrated potentiometrically with perchloric acid. Concentration of all amino groups [amino] was obtained.

Concentrations of primary, secondary, and tertiary amino groups separately were determined using the reaction of PEi-g-PA12 with phthalic acid [ ].

### Determination of solution viscosity

Solution viscosity  $\eta_{\text{rel}}$  (relative viscosity) was determined using a 0.005 g/ml solution of graft polymer in m-cresol at  $25^{\circ}\text{C}$  as in DIN 53727/ISO 307. For determination of characteristic viscosity  $[\eta]$ ,  $\eta_{\text{rel}}$  of 0.01–0.11 g/mol solutions of graft polymer was measured, and viscosity number  $\text{VN} = (\eta/\eta_0 - 1)/C_p$  (where  $\eta$  = viscosity of the polymer solution,  $\eta_0$  = viscosity of the solvent,  $C_p$  = concentration in g/ml of the polymer in the solution) was plotted against  $C_p$  and approximated to 0 (Fig. 4).

### Gel permeation chromatography (GPC)

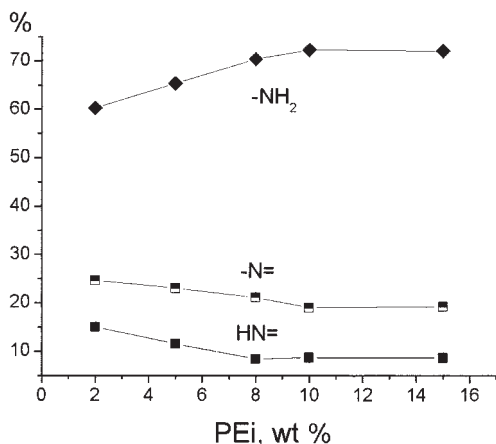
GPC experiments were fulfilled using Agilent chromatograf with PFG of PSS column and PSS WINGPC software.

Samples were dissolved in hexafluoroisopropanol with 0.02 sodium trifluoroacetate in the amount of 5 g/l under room temperature. The rate of the mobile phase was 1 ml/min; detection was by the refraction index, according to PMMA as a standard.

An attempt to solve samples in a hexafluoroisopropanol-toluene mixture was made. Only for sample PEi-g-PA12 (2 wt %) was a strong enough signal obtained. For samples with 5, 8, 10, and 15 wt % of PEi, signals were very weak and could not be used for

**TABLE II**  
**Concentration of Amino Groups in PEi-g-PA12 Samples (with Different Amounts of PEi) on the Results of IR-Spectroscopy and End Group Titration**

Sample	PEi, wt %	[amino], mmol/kg titration data	IR-spectr. data	Titration data		
			[NH <sub>2</sub> ], mmol/kg	[-NH <sub>2</sub> ], mmol/kg	[NH=], mmol/kg	[-N=], mmol/kg
8	2	365	328	220	55	90
9	5	780	635	510	90	180
10	8	1250	870	880	105	265
11	10	1445	1060	1045	125	275
12	15	2080	1310	1500	180	400



**Figure 1** Primary, secondary, and tertiary amino groups % ratio on the amount of PEi in PEi-g-PA12.

calculations. Samples with the highest PEi content (30 and 40 wt %) were not soluble in the above-mentioned solvent mixture. All samples exhibited satisfactory solubility in pure hexafluoroisopropanol.

### Melt rheology

Rheology in melt was investigated with Dynamics spectrometer RDAIII (Reometrics) according to ASTM D4440. Samples (plates  $d = 25$  mm,  $h = 0.4$  mm) were dried, melted, and loaded with a frequency sweep of  $0.1 - 400 \text{ sec}^{-1}$ . The experiment was carried out under 200, 220, 240, and  $260^\circ\text{C}$ .

### Dynamic mechanical thermal analysis (DMTA)

DMTA was made with a 10 TSA-Plots device, heat rate was  $1\text{K}/\text{min}$ , frequency of loading  $1 \text{ Hz}$ , temperature interval from  $-180$  to  $180^\circ\text{C}$  according to DIN EN ISO 6721 Part 2 SAA 0664. Samples were compression

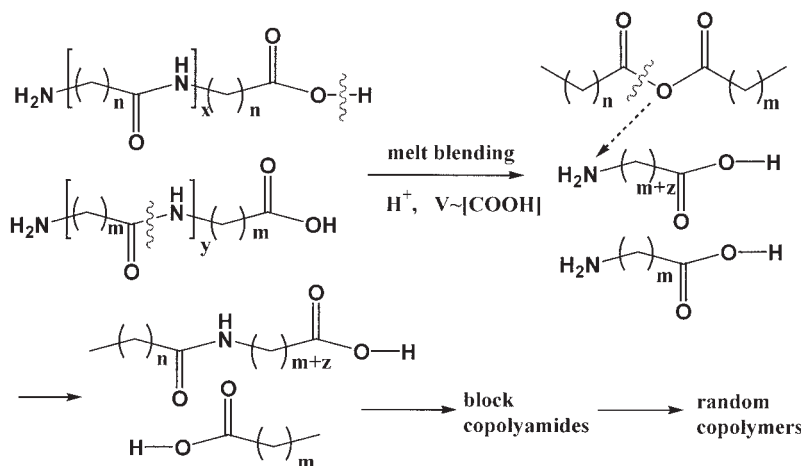
molded (5 min/ $220^\circ\text{C}$ ), punched, and dried  $> 72$  h at  $60^\circ\text{C}$  in a vacuum chamber.

## RESULTS AND DISCUSSION

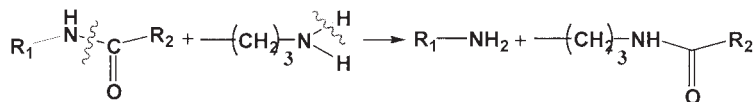
It is known that during melt blending of two amides, an interchange reaction occurs, leading to the formation of block copolymers, followed by the formation of random copolymers (with increasing duration of blending),<sup>10</sup> Scheme 2. The reaction is catalyzed by  $\text{H}^+$  ions, and its rate is proportional to the first power of the carboxyl groups' concentration. The distribution of products in the acidolysis of mixed amides indicates that the mechanism of interchange involves the formation of an anhydride and an amine from a carboxyl group and an amide. The reverse reaction results in the original products on a statistical basis. Aminolysis of an amide does not occur at a significant rate in the absence of carboxyl groups; the direct carboxyl-catalyzed reaction of an amine with an amide can also be involved, especially if the amine concentration is high.

Oenbrink and colleagues<sup>8</sup> assumed, according to the results of end group titration and molecular weight measurements, that during the melting of a polyamide in the presence of amino terminated dendrimer molecules, under the influence of the amino groups of the core molecule, chain rupture occurs at the amide groups in the polyamide chain. The fragment containing the carboxyl group reacts with an amine terminal group of the core molecule, while the other chain fragment is amine-terminated (according to Scheme 3):

This reaction repeats until all free amino groups of the core molecule are occupied. According to Borggreve et al.,<sup>7</sup> since rupture can occur at any place in the chain, there will be a wide spread in the lengths of the nylon chains of the star-branched polymer, by which it is distinguished from the star-branched nylons pre-



**Scheme 2** Interchange reaction in polyamide blends.<sup>11</sup>



Scheme 3. Chain rupture in polyamide polyamide blends.<sup>7</sup>

pared according to the state of the art by controlled chain growth on the core molecule, which would show a relatively narrow molecular weight distribution.

de Brabander et al.<sup>5</sup> reported that star-branched polycaprolactone synthesized from linear caprolactone and a second generation of polypropylenimine dendrimer as a core, as well as the sample obtained by polymerization of caprolactone initiated by this dendrimer, have the same intrinsic viscosity. Star nylon-6 was synthesized using linear polyamide 6 and amino terminated polypropylenimine dendrimer (four end groups).

According to published works,<sup>5,7</sup> reaction transamidation seems to be a very suitable and fast way for synthesis of star-branched polycondensates, including polyamides. In these papers, preference was given to dendrimer structures as core molecules, which is not accessible for production scale.

### Investigations on peculiarities of grafting PA12 onto PEi core molecules

In the present work, synthesis and characterization of star-branched polyamide 12, grafted onto PEi cores, are described. PEi (Scheme 1, a) is a highly branched polyamine, obtained by aziridines polymerization or by acid catalyzed polymerization of the monomer ethylenimine. Nitrogen containing units are in the approximate ratios of 25–46% - primary amino groups, 30–45% - secondary, 16–40% - tertiary.<sup>11</sup>

Synthesis of PEi-g-PA12 was fulfilled in two ways: ring-opening polymerization of LL with subsequent reaction transamidation of linear polylauro lactam in the presence of PEi as a one pot reaction, or by direct reaction transamidation of linear polylauro lactam in the presence of PEi (Scheme 1, b).

Preliminary investigations of the transamidation reaction were fulfilled in laboratory conditions. Linear polylauro lactam was melted, and PEi (50% aqua solution) was added in the amounts of 4–30 wt %. Melt viscosity, which is proportional to torque, changes extremely during the process (Fig. 2). The rapid increase period is followed by a slower decrease one, which continues about 3–3.5 hours, after which equilibration seems to be established. This could be an indirect evidence that the transamidation reaction takes place. Houben-Weyl<sup>11</sup> investigated the kinetics of the transamidation process in PA66/PA6I blends. Curves of transamidation degree and degree of ran-

domness as a function of extrusion time, show rapid (20 min) and slow (until 2.5 h and more) periods.

Concentrations of amino and carboxyl end groups, as well as solution viscosity of PEi-g-PA12 samples I–IX, prepared at the lab scale, and samples prepared at the larger scale belong to the same value area 15 February 2005 (Table III).

Concentration of all types of amino groups depends on the concentration of core PEi molecules and increases linearly with a growing PEi amount. Concentrations of primary, secondary, and tertiary amino groups, determined independently, also grow linearly with PEi content (Table I, Fig. 3), whereas % ratio between amino groups of different types changes. Percent of primary amino groups increases in samples proportionally to the concentration of PEi (until 8–10 wt % of PEi) (which corresponds to 1250–1400 mmol/kg of total amino groups). The % of secondary and tertiary ones decrease correspondingly (Fig. 1).

If only end primary amino groups of PEi take part in reaction transamidation, then the ratio between all kinds of amino groups should not change. Therefore, it seems reasonable that when the concentration of PEi is  $\leq 8$  wt %, some part of the secondary and tertiary amino groups of PEi also serve as arm-forming centers.

To confirm the hypothesis about participation of secondary amino groups in the grafting reaction, bis(hexamethylen)tri amin BHMT was used as a model grafting agent, which has only primary and secondary amino groups. Samples of PA12 grafted onto BHMT (samples XI–XIV) were then brought into contact with PHA, which was taken in excess according to all

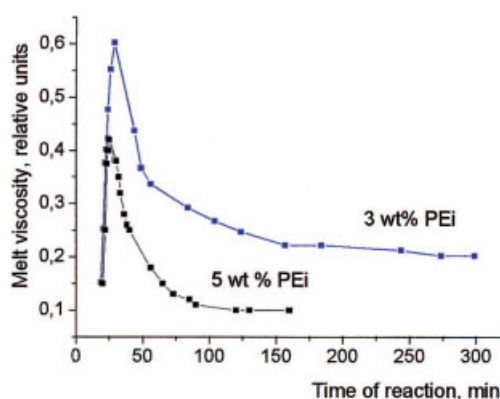


Figure 2. Changing of melt viscosity during transamidation reaction of PA12 in the presence of PEi.

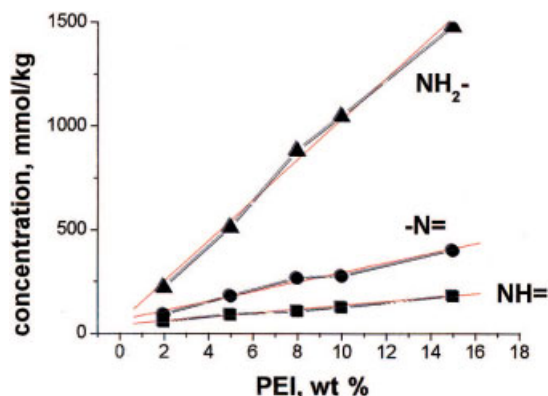
**TABLE III**  
**Solution Viscosity  $\eta_{rel}$ , End Groups Concentration, and Melt and Glass Transitions of PEi- g-PA12 Samples, Prepared by Ring-Opening Polymerization of LL or Transamidation of PA12 with Different Concentration of Core (PEi) Molecule**

N	Sample	$\eta_{rel}$	[-COOH], mmol/kg	[amino groups], mmol/kg	DSC	
					T <sub>g</sub> , °C	T <sub>m</sub> , °C
I	LL//PEi (2 wt %)	1.53	5	345	32	167–177
II	PA12//PEi (2 wt %)	1.47	3	363	35	170
III	LL//PEi (5 wt %)	1.26–1.27	4–5	824	24	174
IV	PA12//PEi (5 wt %)	1.25	7	775–782	31	174
V	LL//PEi (8 wt %)	1.2	2	1260–1269	19	170
VI	PA12//PEi (8 wt %)	1.2	5	1247–1254	18	169
VII	LL//PEi (10 wt %)	1.18	6–8	1516–1553	14	167
VIII	PA12//PEi (10 wt %)	1.17	4–5	1410–1448	16	167
IX	PA12//PEi (15 wt %)	1.14	10–11	2079–2082	10	159
X	PA12	1.61	72	68	40	178

amino groups in these samples. Data in Table II show that all amino groups in samples XI– XIII react with PHA ([amino] after reaction with PHA is low). An exception is sample XIV, for which it seems that the amount of PHA was not enough to react with all secondary amino groups. Part of the PHA was lost during the reaction due to sublimation. (It is supposed that [amino] after reaction with PHA = 34 mmol/kg is unreacted secondary amino groups.) Secondary amino groups with PHA form phthalamido acid, which amount can be measured by titration. Therefore, the rest of the carboxylic groups [-COOH]<sub>f</sub> after purification is equal to the secondary amino groups [NH=] that didn't take part in grafting. As the ratio of primary and secondary amino groups in BHMT is 2 : 1, then the [-COOH]<sub>f</sub> = [NH=] after reaction with PHA should be expected to be in the amount of 1/3 the initial content of [amino] if secondary amino groups don't take part in the grafting process. But from data in Table IV, it is clear that about 50–70% of the secondary amino groups take part in grafting. Thus, the decrease of [NH=] in the amino group ratio in PEi-g-

PA12 samples with different content of PEi can be explained by participation of the secondary amino groups in the grafting reaction. [-NH<sub>2</sub>] after reaction with PHA, determined by IR-spectroscopy (Table IV), is in good accordance with that one calculated as [-NH<sub>2</sub>] = [amino]<sub>0</sub> - [NH=].

For explanation of the % decrease of tertiary amino groups in PEi-g-PA12 samples with the increase of PEi content, grafting of PA12 was carried out in the presence of tris(2- aminoethyl)amine TAEA, a model branching agent with primary and tertiary amino groups in the ratio of 3 : 1. Branched samples were treated with an excess of PHA, purified, and investigated. The rest of [amino] after reaction with PHA (Table V), which is equal to the tertiary amino groups in samples XV and XVI, is lower than the calculated initial amounts of [-N=] in the polymer samples. Moreover, the rest of [-COOH] in these samples after reaction with PHA and purification is much higher than could be expected, as there should not be any carboxylic groups left (Table VI). Accordingly, the [-NH<sub>2</sub>] after reaction with PHA, on IR-spectroscopic data, is somewhat higher as it was calculated as [-NH<sub>2</sub>] = [amino]<sub>0</sub> - [N=]. According to these data, it seems that about 10–30 % of tertiary amino groups transform into another structure, which explains the decrease of the [-N=] % ratio in PEi-g-PA12 samples (Fig. 1).



**Figure 3** Dependence of primary, secondary, and tertiary amino groups concentration on the amount of PEi in PEi-g-PA12.

### Gel permeation chromatography (GPC)

GPC measurements show the increase in molecular weight of samples with 2 wt % of PEi and subsequent decrease of these values with increase of PEi content. This phenomenon can be reasonably explained by interaction of two factors, which are degree of branching and length of "arms." In cases of low concentration of the branching agent, the degree of branching is low and the length of arms is still big, in which case

**TABLE IV**  
**Primary and Secondary Amino Groups Concentration in Samples of PA12 Branched in the Presence of Bis(hexamethylenetriamin) BHMT on the Results of Titration and IR-Spectroscopic Measurements**

N	[-NH <sub>2</sub> ], mmol/kg, data on IR-spectroscopic measurements	[-NH <sub>2</sub> ]=[amino] <sub>0</sub> -[NH=], mmol/kg	[NH=] <sub>0</sub> before reaction with PHA, mmol/kg	[NH=] after reaction with PHA, mmol/kg	NH= reacted, %
XI	148–170	187 – 20 = 167	187/3 = 62	20	69
XII	152–162	171 – 23 = 148	171/3 = 57	23	60
XIII	323–332	345 – 57 = 288	345/3 = 115	57	50
XIV	459–497	555 – 25 = 530	555/3 = 185	25 + 34	68

**TABLE V**  
**Amino [amino] and Carboxylic [-COOH] Groups Concentration in Samples of PA12 Branched in the Presence of Ris(2-Aminoethyl)amin TAEA Before and after Reaction With Phthalic Acid PHA and after Purification (Extraction and Reprecipitation) on the Results of Titration. [COOH] before Reaction with PHA for Samples XV–XVI < 5 mmol/kg**

N	TAEA used for PA12 branching, wt %	[amino] <sub>0</sub> before reaction with PHA, mmol/kg	[amino] after reaction with PHA, mmol/kg	[COOH] after reaction with PHA, mmol/kg	[COOH] after purification, mmol/kg
XV	1.5	335–341	75	66	46
XVI	3.0	622–640	111	192	57

**TABLE VI**  
**Primary and Tertiary Amino Group Concentration in Samples of PA12 Branched in the Presence of Tris(2-aminoethyl)amin TAEA before and after Reaction With Phthalic Acid PHA, on the Results of Titration and IR-Spectroscopic Measurements**

N	[-NH <sub>2</sub> ], mmol/kg, data on IR-spectroscopic measurements	[-NH <sub>2</sub> = [amino] <sub>0</sub> - [N=], mmol/kg	[-N=] <sub>0</sub> before reaction with PHA, mmol/kg	-N = reacted, %
XV	348	348–75 = 273	338/4 = 84,5	11.2
XVI	590	630–111 = 519	630/4 = 157,5	29.5

**TABLE VII**  
**Number Average Mn, Weight Average Mw Molecular Weights, and Molecular Weight Distribution of PEi-g-PA12 Samples D<sub>star</sub> and PA12 “arms” D<sub>arm</sub>, f – number of “arms”**

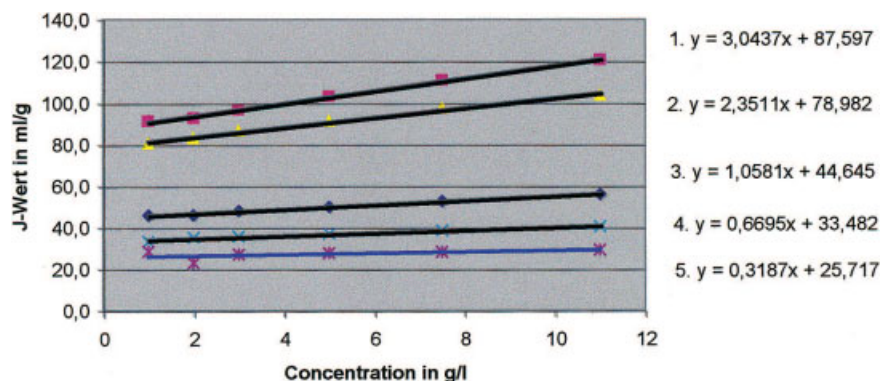
Sample	Mn g/mol	Mw g/mol	D <sub>star</sub>	f	D <sub>arm</sub>
PA12	8,100	18,000	2.22	-	-
LL//PEi (2 wt %)	16,600	27,900	1.68	3.24	3.20
LL//PEi (5 wt %)	11,200	15,500	1.38	7.50	3.85
LL//PEi (8 wt %)	9,700	13,500	1.39	12.94	6.05
LL//PEi (10 wt %)	8,950	13,000	1.46	12.59	8.17
PA12//PEi (2 wt %)	16,200	28,600	1.77	3.24	3.50
PA12//PEi (5 wt %)	9,700	15,000	1.55	7.50	5.10
PA12//PEi (8 wt %)	8,100	12,500	1.55	12.94	8.10
PA12//PEi (10 wt %)	7,300	10,800	1.49	12.59	8.60
PA12//PEi (15 wt %)	5,900	8,900	1.50	22.06	12.03
PA12//PEi (30 wt %)	8,100	13,200	1.62		
PA12//PEi (40 wt %)	7,700	12,600	1.65		

Both D<sub>star</sub> and D<sub>arm</sub> depend on PEi content. Till about 10 wt % of PEi narrowing of the D<sub>star</sub> occurs. With further increase of PEi content D<sub>star</sub> tends to grow. D<sub>arm</sub> grows with PEi content which can be explained by increase of number of “arms”.

the increase of molecular weight of the grafted sample compares to the linear PA12, while increase of PEi content causes the increase of the degree of branching and the correspondent shortening of the arms' length.

Molecular weight distribution for grafted samples D<sub>star</sub> is considerably lower than for the linear polymer, which was also pointed out by de Brabander et al.<sup>5</sup> According to them, molecular weight distribution is a





**Figure 4** Solution viscosity measurements of PEi-g-PA12 samples with (1) 2 wt %, (2) 5 wt %, (3) 8 wt % (4) 10 wt %, (5) 15, 30, and 40 wt % of PEi.

function of the number of arms and can be expressed by the following equation:

$$D_{\text{star}} = (D_{\text{arm}} + f - 1)/f,$$

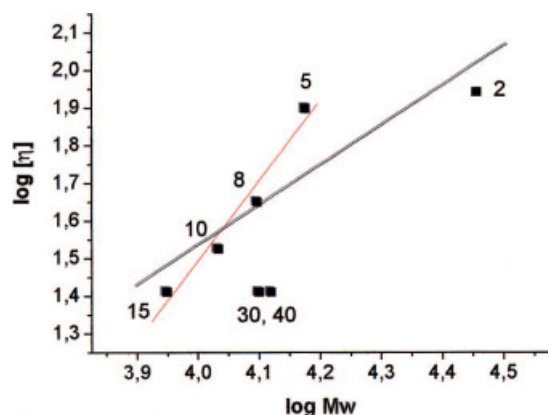
where  $f$  = number of arms and  $D_{\text{arm}}$  = molecular weight distribution of "arms".

As  $f$  can be calculated as the ratio between the concentration of the primary amino groups that are the end functional groups of the arms and the concentration of the primary amino groups in linear PA12,  $D_{\text{arm}}$  was calculated for all PEi-g-PA12 samples (Table VII).

Both  $D_{\text{star}}$  and  $D_{\text{arm}}$  depend on PEi content. Until about 10 wt % of PEi, narrowing of the  $D_{\text{star}}$  occurs. With further increase of PEi content,  $D_{\text{star}}$  tends to grow.  $D_{\text{arm}}$  grows with PEi content, which can be explained by increase of the number of arms.

### Solution viscosity

Solution viscosity  $\eta_{\text{rel}}$  is lower with respect to the corresponding viscosity of linear PA12, and continues



**Figure 5** Double logarithmic plots of  $[\eta]$  versus Mw for PEi-g-PA12 samples with 2, 5, 8, 10, 15, 30, and 40 wt % of PEi.

to decrease with growing PEi content (Table III, Fig. 4), which is in accordance with data received by de Brabender et al.<sup>5</sup> From data in Figure 1, it can be seen that there is a leap in viscosity value between samples with 5 and 8 wt % of PEi, which can be explained by the sharp shortening of PA12 arms.

Attempts to estimate  $K$  and  $\alpha$  parameters in the Mark-Houwink relationship were made. In Figure 5 double logarithmic plots of  $[\eta]$  versus Mw for all the range of PEi-g-PA12 samples are shown. The linearization procedure gives the best results for samples with 5–15 wt % of PEi (Table VIII). If the sample with 2 wt % of PEi were taken into account, the values of  $K$  and  $\alpha$  differ significantly. Points 30 and 40 in Figure 5 correspond to 30 and 40 wt % of PEi, and they were not taking in linearization, as it is clear from GPC measurements that PEi-g-PA12 with such a high content of PEi would have an unexpected increase of Mw and Mn values. According to data in Table VIII, PEi-g-PA12 samples with 5–15 wt % of PEi have a shape of semi coils.

### Thermal characteristics

Samples of PA12-g-PEi were investigated by differential scanning calorimetry (DSC) to see changes in the

**TABLE VIII**  
Parameters  $K$  and  $\alpha$  in Mark-Houwink Relationship for PEi-g-PA12 Samples; Data for Linear PA12 Are Given for Comparative Purposes

Samples	$K$ * $10^{-4}$	$\alpha$	Coefficient of correlation
Linear PA12	8.4	0.68	
PEi-g-PA12 samples with 5–15 wt % of PEi	0.00095	1.06	0.979
PEi-g-PA12 samples with 2–15 wt % of PEi	19.6	2.13	0.891

**TABLE IX**  
**Melt Viscosity of PEi-g-PA12 with 5 wt % of PEi Under**  
**Different Temperatures and a Load with a Frequency**  
**Sweep 0.1–400 c<sup>-1</sup>**

Temperature, °C	200	220	240	260
Melt viscosity, Pa.s	25	18	9	5

melting and crystallization behavior depending on the degree of branching.

Glass transition temperatures and melting point of samples decrease sufficiently with increase of PEi content until 15 wt % (Table III), whereas samples with low PEi content don't exhibit noticeable changes in thermal characteristics, as was also mentioned by de Brabander et al.,<sup>5</sup> where the authors used 0.5–1.0 wt % of core dendritic molecules.

### Melt rheology

Melt viscosity of PEi-g-PA12 samples is significantly lower than the one for linear PA12 with approximately the same molecular weight, that is, melt viscosity of PEi-g-PA12 with 5 wt % of PEi under load with a frequency sweep 0.1–400 c<sup>-1</sup> and 200°C is 25 Pa.s (Table IX), whereas melt viscosity of linear PA12 under the same conditions is 200 Pa.s. Such a drastic fall of viscosity was also reported by others<sup>5, 7, 8</sup> and is characteristic of the formation of a star-branched nylon. Viscosity of linear and star-branched polymers don't change in the range of applied load.

### Mechanical characterization

DMTA measurements provide a glass transition of PEi-g-PA12 samples. According to received data, the glass transition temperature of star polymers decreases with increase of PEi content and is significantly lower than T<sub>g</sub> for linear PA12 (f.e. T<sub>g</sub> (PA12) = 49.8°C; T<sub>g</sub> (PEi-g-PA12, 3 wt % PEi) = 38.5°C; T<sub>g</sub> (PEi-g-PA12.5 wt % PEi) = 31.5°C), while other authors<sup>5, 7</sup> reported no differences in T<sub>m</sub> and T<sub>g</sub> of linear and star-branched nylons.

### CONCLUSION

Synthesis of PEi-g-PA12 with concentration of PEi 2–40 wt % was fulfilled in two different ways, as

ring-opening polymerization of LL and as transamidation of linear PA12 in the presence of core PEi molecules. Evidence that the grafting process occurs has been obtained. Both methods provide almost uniform materials. Participation of not only the primary but also the secondary and tertiary amino groups in the formation of PEi-g-PA12 polymers (until 2–8 wt % of PEi content) have been established. At higher content of PEi (8–15 wt %), only the primary amino groups of the core molecules take part in grafting.

The obtained material was characterized using different techniques. Decrease of solution and melt viscosity were examined for dependence on PEi content. Molecular weight and molecular weight distribution of star polymers and PA12 "arms" with different content of cores, as well as melt and glass transitions, were determined.

The one pot process, including ring-opening polymerization of LL in the presence of PEi cores, provides a convenient method for synthesis of star-branched polymers. Variation of the content of the core molecules gives a possibility of changing a wide range of thermal and viscous properties. PEi-g-PA12 can be proposed for use as a polymer additive for the injection molding process. Due to a high functionality, it can also be an interesting object for further chemical modifications.

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