Method for the Determination of Primary, Secondary, and Tertiary Amino Groups in Star-Shaped Polyamide 12 with a Poly(ethylene imine) Core

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ABSTRACT: A star-branched poly(ethylene imine)-*g*-polyamide 12 with a high concentration of primary amino end groups is an object of interest for future chemical modifications. In many cases, the concentration of primary amino groups, which are also the end groups of the polyamide 12 arms, and the concentrations of secondary and tertiary amino groups in a sample need to be known independently. Because of the difference in the reactivity of phthalic acid toward amino groups, its reaction with poly(ethylene imine)-*g*-polyamide 12 can be used for the analytical determination of these groups. With primary amino groups, phthalic acid forms phthalimido moieties, which are detectable by IR spectroscopy. The IR bands can be used for quantitative analysis with an appropriate calibration procedure. The concentration of primary amino groups can also be calculated as the difference between the concentration of all types of amino groups before the reaction with phthalic acid and the final concentration of amino and carboxylic groups after the reaction. The final concentration of the amino groups is equal to the concentration of unreacted tertiary amino groups after the reaction with phthalic acid anhydride. The difference between the final concentration of carboxylic groups and the initial concentration of carboxylic groups is equivalent to the concentration of secondary amino groups, which react with phthalic acid to form phthalamido acid moieties. J Appl Polym Sci 95: 556–563, 2005

Key words: branched; FT-IR; polyamides; polyimines; star polymers

INTRODUCTION

Star-shaped poly(ethylene imine)-*g*-polyamide 12 (PEi-*g*-PA12) can be synthesized by the ring-opening polymerization of laurolactam (LL) or by the transamidation reaction of a linear polylaurolactam [polyamide 12 (PA12)] in the presence of poly(ethylene imine) (PEi) as a core molecule (Fig. 1). The synthesis has been described in detail in patents.[1,2]

PEi is a highly branched polyamine (obtained by aziridine polymerization or the acid-catalyzed polymerization of the monomer ethylenimine). It is composed of units that have two carbon atoms per nitrogen, and these units are randomly distributed in approximate concentrations of 25–46% primary amino groups, 30–45% secondary amino groups, and 16–40% tertiary amino groups[3] (Fig. 1). This distribution gives rise to what is believed to be a spheroid polymer molecule that is composed of many branched segments, with the tertiary amino nitrogens being the branching sites and the primary amino nitrogens being the terminal groups of each segment. The primary and secondary amino nitrogens are reaction sites by which PEi can be conveniently modified. After the reaction of PA12 with PEi, ratios of different amino groups should also be found in PEi-*g*-PA12.

Highly branched PEi-*g*-PA12 belongs to the class of star-branched polyamides, which are, despite their other interesting properties,[1,4–6] objects of interest for future chemical modifications. For many chemical modifications, it is important to know the concentration of primary amino groups, which are also the end groups of the PA12 arms. Therefore, the concentrations of the primary, secondary, and tertiary amino groups in a sample are worth knowing.

The usual procedure of determining the amino group concentration in polyamides is the potentiometric titration of an *m*-cresol solution with perchloric acid.[6] This or another titration method[7] gives the concentration of all amino groups in a sample and does not distinguish between the concentrations of primary, secondary, and tertiary amino groups.

The proposed method of separately determining primary, secondary, and tertiary amino group concentrations is based on the difference in the reactivity of phthalic acid (PHA; or phthalic anhydride) toward primary, secondary, and tertiary amino groups. Primary amino groups react with phthalic anhydride through the formation of phthalimido groups (I). With secondary amino groups, phthalamido acid (II) is

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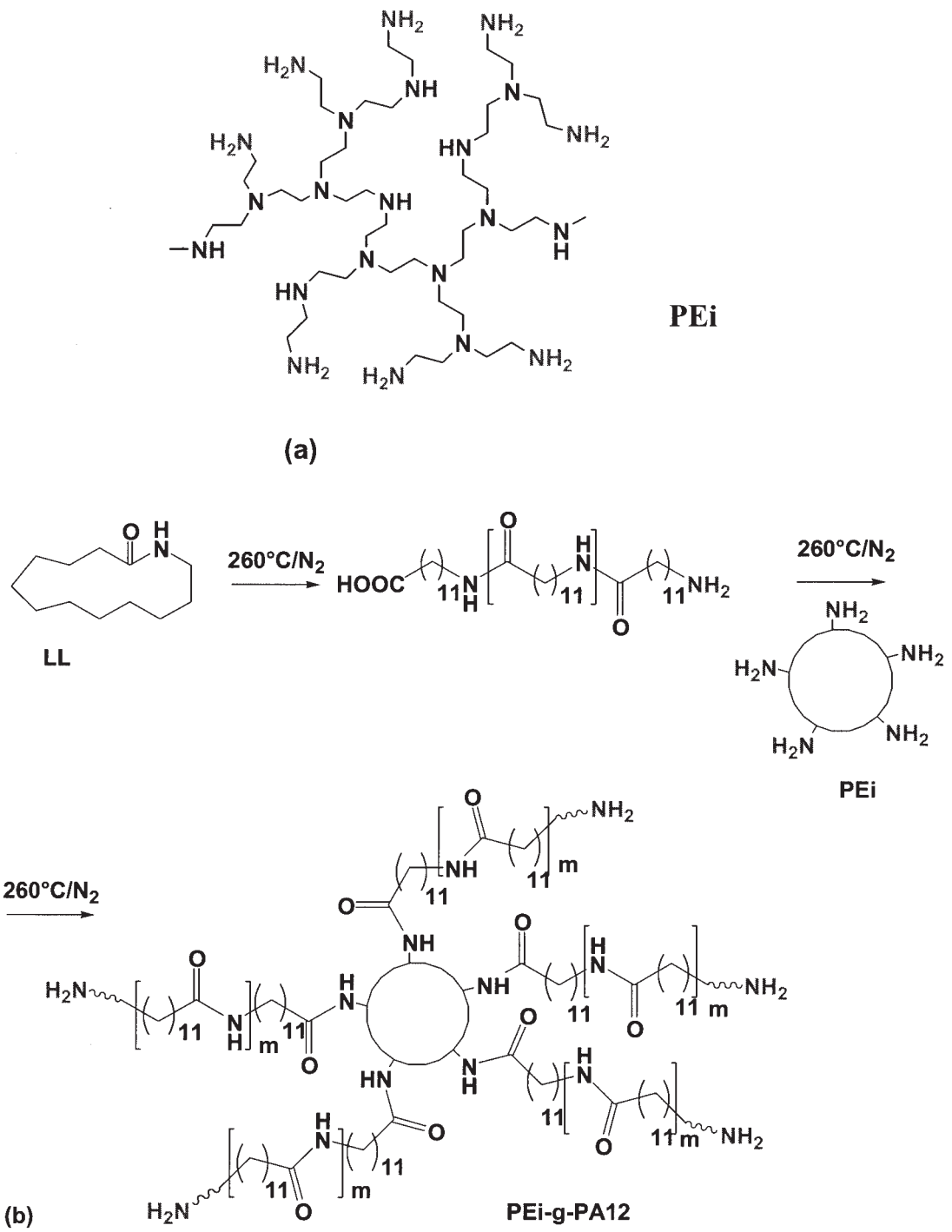

Figure 1 (a) PEi and (b) synthetic scheme of star-branched PA12 from LL or polylaurolactam and a multifunctional core molecule (PEi).

formed, and tertiary amino groups will not react with PHA (Fig. 2).

As mentioned previously, the treatment of PEi-*g*-PA12 samples with equimolar (with respect to the concentration of all amino groups) amounts of PHA will result in the formation of a phthalimide functionality with end primary amino groups and phthalamide acid with secondary amino groups; an unreacted amount of PHA will correspond to the tertiary amino groups of the samples.

Phthalimide moieties are quite detectable by IR spectroscopy. Two characteristic bands (phthalimide I, 1775 cm^{-1}, and phthalimide II, 1725 cm^{-1}), which belong to ν_s and ν_{as} vibrations[8] of this functionality, do not overlap with the PEi-*g*-PA12 band. This gives an outstanding possibility for a quantitative analysis. Therefore, the de-

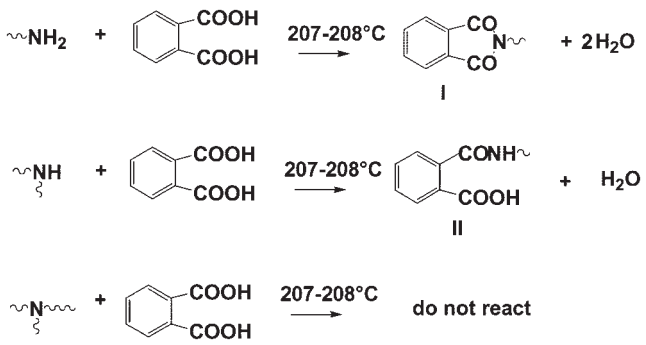

Figure 2 Synthetic scheme of the PHA reaction with primary, secondary, and tertiary amino groups.

termination of the primary amino group concentration is a question of the appropriate calibration procedure and the accuracy of the measurements.

EXPERIMENTAL

Materials

PEi (Lupasol G 100; 50% aqueous solution) was acquired from BASF AG (Ludwigshafen, Germany). PHA (99.5%; Fluka, Buchs, Switzerland), 4,4′-diamindicyclohexylmethane (PACM), ethanol, *N*-methyl-2-pyrrolidone and (NMP; 99.5%; Merck, Darmstadt, Germany) were used as received. LL was available from Degussa AG (Germany).

IR spectroscopy measurements

For the IR investigations, a Nikolet 5 DXC Fourier transform infrared (FTIR) spectrometer was used. The polymer samples were measured in thin layers between two NaCl plates.

For the sample preparation, the polymer samples were melted between two NaCl plates and cooled.

Determination of the amino and carboxylic groups by titration

The concentration of all amino groups ([amino]) was measured potentiometrically in distilled *m*-cresol with a 0.1 mol/L perchloric acid/ethanol solution.

The concentration of carboxylic groups was measured by titration in hot benzyl alcohol at 180°C with a 0.1 mol/L potassium hydroxide solution in ethylene glycol. Indication was done colorimetrically with phenolphthalein. Calibration was performed with benzoic acid.

Synthesis of linear amino-terminated PA12 as a model compound for quantitative IR spectroscopy analysis

LL (50.68 mol) was melted in a heating vessel from 180 to 210°C and was transferred into a pressure-tight polycondensation vessel to which 10–200 ppm of the catalyst (reducing and nonreducing phosphoric acids) and 4.14 mol of PACM were added. The temperature was increased to 280°C, and the ring-opening polymerization of LL was conducted under 22 bar for 4 h. Then, the pressure was slowly reduced to 1 bar, and the process was continued for 4 h under a flow of N_2. The melt was discharged, cooled, and pelletized. The initial NH_2 concentration was 700 ± 30 mmol/kg, and the initial COOH concentration was 4 mmol/kg.

Reaction of linear amino-terminated PA12 with PHA

Samples of synthesized linear amino-terminated PA12 (0.08 kg) were mixed with 1.23–9.85 g of PHA (2–16 mol %, based on LL; Table I). The reaction was conducted in a Duran 50 glass tube at 207–208°C under N_2 with stirring for 5 h. The temperature was set at this value, as the degradation of phthalic anhydride (which was formed from PHA when the temperature increased above 140°C) at a higher temperature had been reported.[9] The melt was discharged and cooled, and the resulting strand was cut. The concentration of amino groups ($[—NH_2]_f$) and the concentration of carboxylic groups ($[—COOH]_f$) in PA12 samples after the reaction with PHA, as well as the calculated concentration of carboxylic groups ($[COOH]_{theor}/2$), caused by different amounts of PHA, are given in Table I.

TABLE I
Some Characteristics of Model Linear PA12 After Reactions with Different Amounts of PHA

Sample	PHA used for the reaction (mol %)	PHA used for the reaction (g)	$[COOH]_{theor}/2$ (mmol/kg)	$[COOH]_f$ (mmol/kg)	$[NH_2]_f$ (mmol/kg)	$\Delta[—NH_2]$ (mmol/kg)
1	2	1.23	91.2	≤5	579.3	120.7
2	4	2.46	179.7	≤5	516.3	183.7
3	6	3.69	265.6	≤5	448.9	251.1
4	8	4.92	349.0	≤5	337.6	362.4
5	10	6.16	430.7	≤5	270.6	429.4
6	12	7.39	509.4	≤5	161.4	538.6
7	16	9.85	660.4	≤5	45.0	655.0

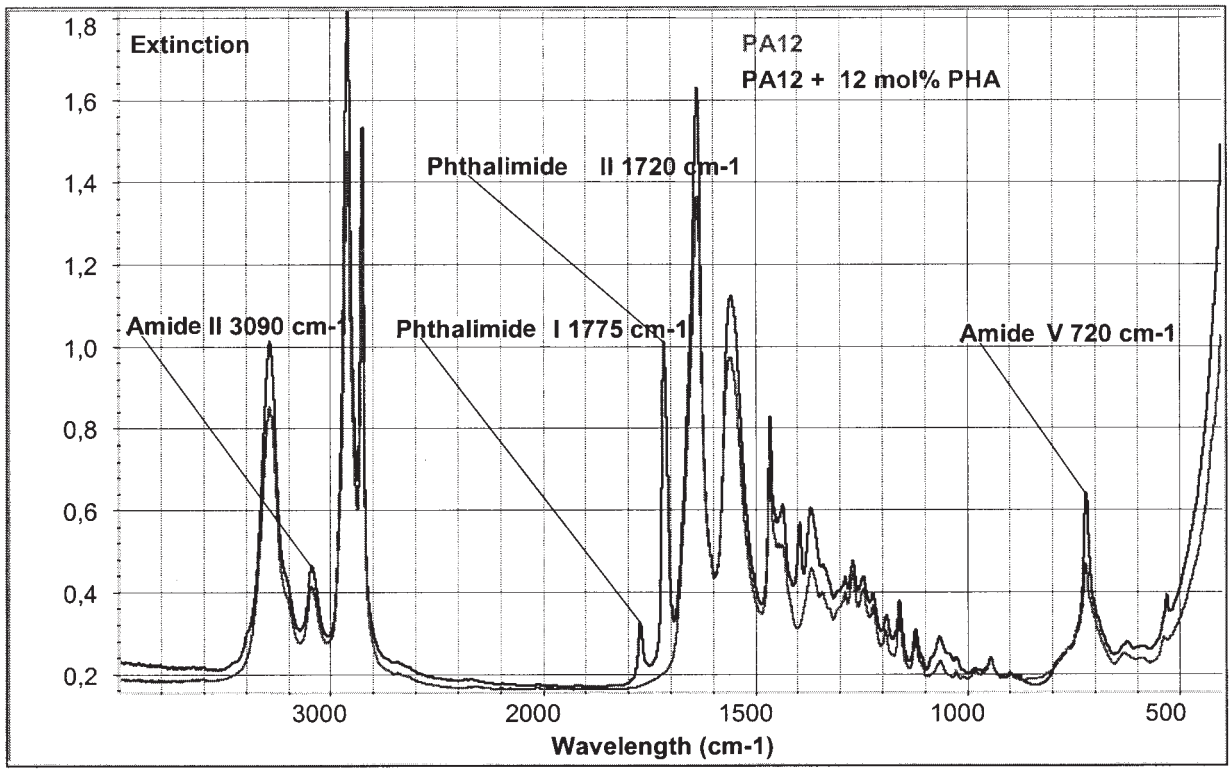

Figure 3 FTIR spectrum of amino-terminated linear PA12 modified with 12 mol % PHA (in a thin layer between two NaCl plates).

Calibration procedure for quantitative IR spectroscopy analysis

As linear PA12 contained only primary amino end groups, it reacted with PHA, forming only phthalimide groups, which were detectable by IR spectroscopy. Therefore, it was suitable as a model compound for the calibration procedure.

IR spectra of PA12 modified with different amounts of PHA (samples 1–7), as well as a spectrum of unmodified PA12, were measured. Examples of IR spectra of amino-terminated linear PA12, unmodified and modified with PHA, are given in Figure 3.

For quantitative calculations and calibration curve creation, the integrated intensities of the phthalimide I and phthalimide II bands, which are characteristic of phthalimide groups, were divided by the integrated intensities of the amide II band (second oberton of $\nu_{C—N}$ and δ_{CNH}, 3090 cm^{-1}) and the amide V band (δ_{NH}, 720 cm^{-1}), which belonged to the vibration of PA12 amido groups[10] (Fig. 3 and Table II). Samples 1–7 of linear PA12 after its reaction with different amounts of PHA were titrated, and $[—NH_2]_f$ and $[—COOH]_f$, as well as the concentration of reacted amino groups ($\Delta[—NH_2] = [—NH_2]_0 - [—NH_2]_f$),

TABLE II
Integrated Intensity of Bands in the IR Spectra of Amino-Terminated Linear PA12 Modified with Different Amounts of PHA

	Integrated Intensity			
Sample	Amide II (3090 cm^{-1})	Phthalimide I (1775 cm^{-1})	Phthalimide II (1725 cm^{-1})	Amide V (720 cm^{-1})
1	10.38	0.19	2.15	16.69
2	12.31	0.68	5.53	20.73
3	13.56	1.24	8.28	23.32
4	10.46	1.01	9.37	17.59
5	8.98	1.02	10.24	14.65
6	8.47	1.60	11.65	14.93
7	9.09	2.02	15.83	16.12

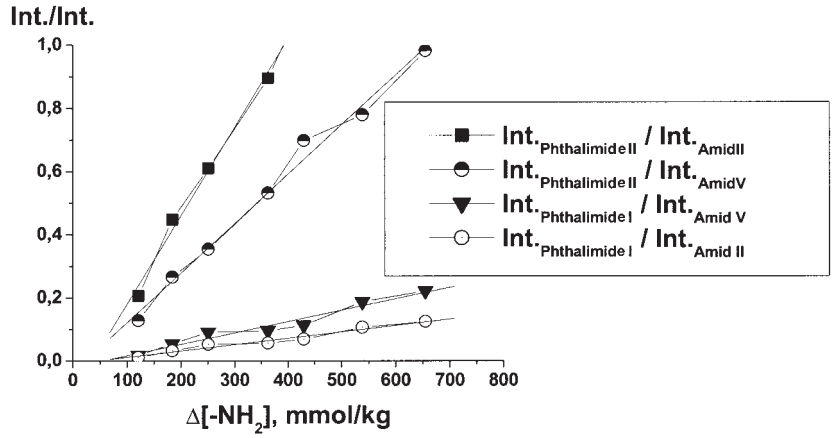

Figure 4 Dependence of the integrated band intensity ratio in IR spectra on Δ[—NH_2] in PA12 samples modified with different amounts of PHA.

were determined (Table I). The previously mentioned ratios were plotted against the reacted amino groups in a sample Δ[—NH_2] (Fig. 4). A linearization procedure gave a high correlation coefficient in each case (0.97–0.99).

Synthesis of PEi-*g*-PA12

LL (8 kg) was melted and transferred into a pressure-tight stainless steel polycondensation vessel with a coil stirrer. Water (500 mL) and a catalyst (10–200 ppm) were added. The cleavage of LL was conducted at 290°C under autogenic pressure for 6 h. The pressure was then slowly reduced to 10 bar, and the temperature was decreased to 265°C. A 50% PEi aqueous solution was added (0.32–2.4 kg), and this resulted in 2–15 wt % PEi with respect to LL (samples 8–12). Stirring was continued for 30 min, the pressure was reduced to 1 bar, and the reaction was conducted for 4 h. The melt was discharged, cooled, and palletized. The concentrations of amino groups in the PEi-*g*-PA12 samples are given in Table III. The initial concentrations of carboxylic end groups ($[COOH]_0$) were 4–6 mmol/kg for all the samples.

Reaction of PEi-*g*-PA12 with PHA

Samples of PEi-*g*-PA12 (with 2–15 wt % PEi; 0.1 kg) were mixed with 7–37 g of PHA (an equimolar amount with a small excess with respect to the concentration of all amino groups in PEi-*g*-PA12; Table IV). The reaction was conducted under the same conditions used for linear PA12, as described previously. During the reaction, a small amount of phthalic anhydride was lost to sublimation. The concentrations of all amino and carboxylic groups in the PEi-*g*-PA12 samples after the reaction with PHA are given in Table I ([amino] and [—COOH] before purification).

Purification of PEi-*g*-PA12 after the reaction with PHA

As for the reaction of PEi-*g*-PA12 with PHA, the last one was taken in an excess, and the reaction products were purified before quantitative analysis.

Reprecipitation of the samples from NMP

The samples (30 g) were dissolved under heating at 180°C and with stirring in 200 mL of NMP, cooled at

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

Sample	PEi (wt %)	[Amino] (mmol/kg, titration data)	IR spectroscopy data for [NH_2—] (mmol/kg)	Titration data		
				[NH_2] (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

TABLE IV
Concentrations of Amino and Carboxylic Groups in PEi-*g*-PA12 Samples (with Different Amounts of PEi) Modified with an Excess of PHA Before and After Purification

			Before purification		After reprecipitation		After extraction	
Sample	PEi (wt %)	PHA (g)	[Amino] (mmol/kg)	[—COOH] (mmol/kg)	[Amino] (mmol/kg)	[—COOH] (mmol/kg)	[Amino] (mmol/kg)	[—COOH] (mmol/kg)
8	2	7	90	76	92	53	85	58
9	5	15	180	147	185	92	154	88
10	8	22	305	189	270	105	260	105
11	10	25	402	202	280	135	275	115
12	15	37	615	322	—	—	400	180

room temperature (with cooling to 110°C, the polymer precipitated), filtered and washed with hot ethanol, and dried in an oven (80°C) overnight.

Extraction of the side products with ethanol

The polymer samples (10 g) were powdered, and 150 mL of ethanol was added in each case. After 5 h of boiling, the samples were filtered and washed with hot ethanol and were dried in an oven (80°C) overnight. The solubility of the samples in ethanol and NMP increased with the PEi concentration.

The concentrations of all amino and carboxylic groups in samples 8–12 after purification are given in Table I.

Determination of the primary, secondary, and tertiary amino group concentrations in PEi-*g*-PA12

IR spectra of samples 8–12 were measured. Two characteristic phthalimide moiety bands in the IR spectra of the samples were observed (phthalimide I, 1775 cm^{-1}, and phthalimide II, 1725 cm^{-1}). These bands did not appear in IR spectra of pure PEi-*g*-PA12 (Fig. 5).

The measurements of the bands of the phthalimide I, phthalimide II, amide II, and amide V intensity and the definition of the intensity ratios (phthalimide I/amide II, phthalimide I/amide V, phthalimide II/amide II, and phthalimide II/amide V) for samples 8–12 were repeated, just as for linear PA12. The concentrations of reacted primary amino groups ($\Delta[NH_2]$) were determined from corresponding calibration curves. It was assumed that all primary amino groups in a sample reacted with PHA ($\Delta[—NH_2] = [—NH_2]$). The phthalimide I and phthalimide II bands, as well as the amide II and amide V bands, were not totally independent of the nearest bands, which belonged to the oscillation of other groups of the PA12 chain. Therefore, the values of the intensity ratio according to all calibration curves were averaged for more precise

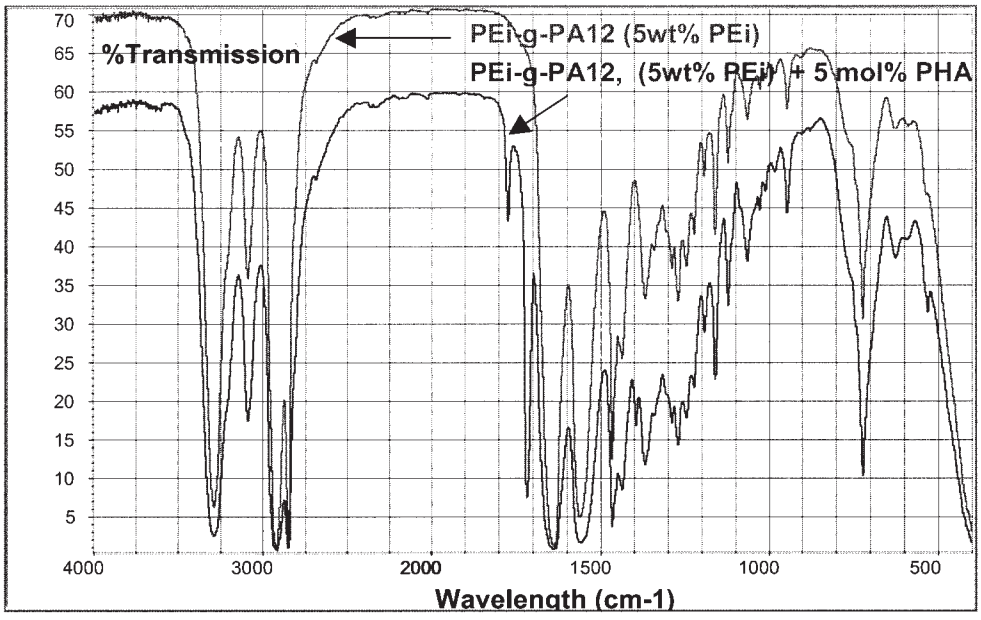

Figure 5 FTIR spectra of PEi-*g*-PA12 unmodified and modified with 5 wt % PHA.

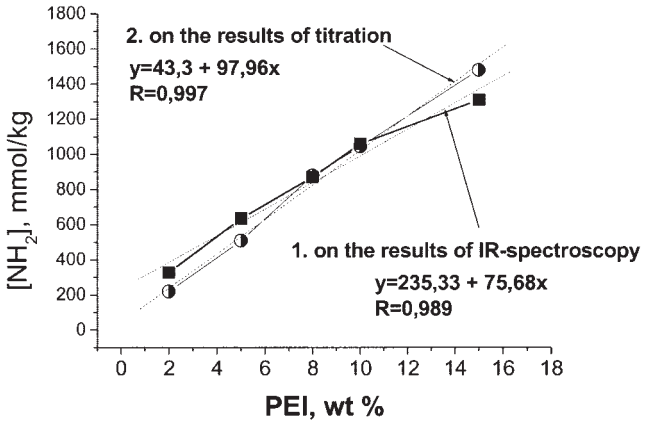

Figure 6 Dependence of the primary amino group concentration on the amount of PEI in PEi-*g*-PA12 (samples 8–12).

results. The —NH_2 concentration, obtained according to all calibration curves (Table IV), was plotted against the concentration of PEi in the PEi-*g*-PA12 samples (Fig. 6, curve 1).

As already pointed out, samples 8–12 had primary, secondary, and tertiary amino groups. As the tertiary amino groups did not react with PHA, the concentration of the remaining amino groups ($[amino]_f$) after the reaction of PEi-*g*-PA12 with PHA and purification was equal to the concentration of tertiary amino groups ([—N═]) in a sample (Table IV).

As previously mentioned, PHA reacted with secondary amino groups under the formation of phthalamido acid II, and this amount could be measured by titration. Therefore, the concentration of the remaining carboxylic groups ($[—COOH]_f$) after purification was equal to the concentration of secondary amino groups ([NH═]) in a sample (Table IV).

Because the concentration of all amino groups was equal to [—NH_2] + [NH═] + [—N═], the concentration of primary amino groups in a sample could also be determined as [—NH_2] = $[amino]_0$ − [—N═] − [NH═] = $[amino]_0$ − $[amino]_f$ − $[—COOH]_f$. The data for the —NH_2 concentration, obtained with only the titration procedure, are shown in Table IV and Figure 6 (curve 2).

RESULTS AND DISCUSSION

The method of determining the primary, secondary, and tertiary amino groups upon the reaction with PHA opened the possibility of determining these group concentrations in polymers.

The primary amino group concentration could be determined from IR spectroscopic measurements of samples after the reaction with PHA. For quantitative analysis, a calibration procedure was necessary. For this purpose, a simple and convenient model compound (PA12) with only primary amino end groups was used, as it formed only phthalimide moieties upon the reaction with PHA. No byproducts were formed. The melt had a color original to that of PA12. Δ[—NH_2] in each case correlated with the calculated concentration of the carboxylic groups formed by PHA ($[—COOH]_{theor}$; Table I). The concentrations of the carboxylic groups after the reaction ([—COOH]) for samples 1–7 were less than or equal to 5 mmol/kg; this was evidence that there was no unreacted PHA in these samples.

The measurements of IR spectra of linear PA12, modified and not modified with PHA (Fig. 3), confirmed that in the spectra of modified PA12 there were two discrete bands, which were not observed in the spectra of unmodified PA12. The measurements of the integrated intensities of the bands of phthalimide I, phthalimide II, amide II, and amide V and the calculations of the phthalimide I/amide II, phthalimide I/amide V, phthalimide II/amide II, and phthalimide II/amide V intensity ratios led to calibration curves (Fig. 4), which showed a linear dependence with a high correlation coefficient between the intensity ratio and Δ[—NH_2].

These calibration curves were used for the determination of the primary amino group concentration in PEi-*g*-PA12. For this purpose, samples of PEi-*g*-PA12 were treated with a small excess of PHA (according to all amino groups in a sample). The purification procedure was performed after the following reaction: (1) extraction with ethanol or (2) reprecipitation from NMP. The sample with 15% PEI was completely soluble in ethanol under boiling; in this case, only the first procedure was used. In all other cases, both methods were carried out, and the results were compared. After and before purification, concentration of all amino groups and the COOH concentration were measured. The data in Table III show that the concentration of amino groups did not significantly change after the purification procedure, except for samples with 10 or 15 wt % PEI, when the solubility of PEi-*g*-PA12 in ethanol was considerable and some of the low-molecular-weight fraction of the polymer was lost. The —COOH concentration always decreased through the washing out of excess PHA.

For samples 8–12, the measurements of the integrated intensities of the bands of phthalimide I, phthalimide II, amide II, and amide V and the calculations of the phthalimide I/amide II, phthalimide I/amide V, phthalimide II/amide II, and phthalimide II/amide V intensity ratios, followed by the determination of the primary amino group concentration according to the calibration curves (Fig. 4), showed that only averaging the —NH_2 concentrations according to all calibration curves produced a sufficient result. This can be explained by some error in the integrated intensity measurements as well as a partial dependence of the in-

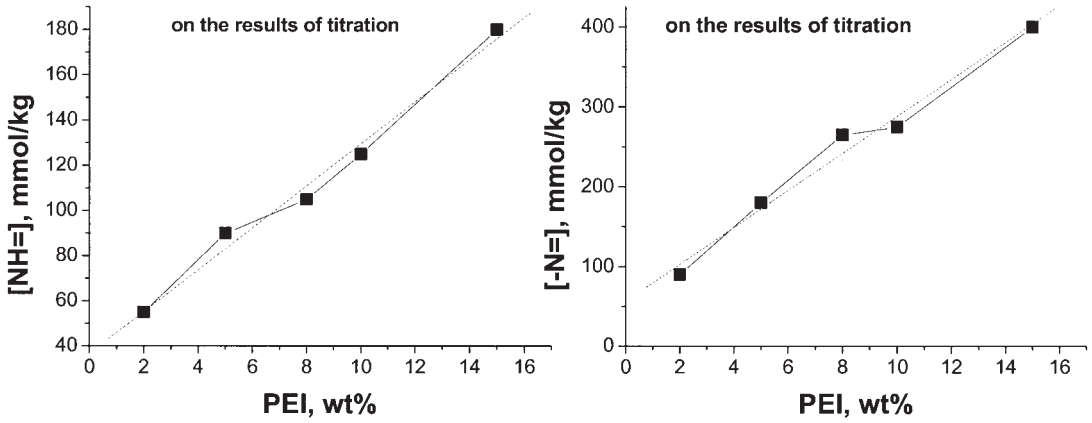

Figure 7 Dependence of the —N═ and ═NH concentrations on the concentration of PEi in PEi-*g*-PA12.

tensity of the used bands on other neighboring bands, which belonged to the oscillation of the PA12 chain.

The —NH_2 concentrations according to IR spectroscopy and titration methods are given in Table III, and they are plotted against the concentration of PEi in PEi-*g*-PA12 samples in Figure 6. These data show the best correlation between IR spectroscopy and titration —NH_2 concentrations for samples 10 and 11. The deviation in the —NH_2 concentrations for sample 12 can be explained by the increased solubility of the polymer and the loss of some low-molecular-weight fractions during reprecipitation, which led to a reduction of the —N═ concentration and a sequence increase in the —NH_2 concentration. For samples 8 and 9, the too high —NH_2 concentration spectroscopic data could be explained by the low intensity of the bands of phthalimide I and phthalimide II, which increased the error of the IR measurements.

The data in Table III and Figure 7 show a linear dependence of the secondary and tertiary amino group concentrations on the PEi concentration in the PEi-*g*-PA12 samples.

Because of the proposed method, the concentrations of primary, secondary, and tertiary amino groups in PEi-*g*-PA12 were determined, and this is important for further possible chemical modifications of this product. According to the plots (Figs. 6 and 7), it is possible to predict the concentrations of amino groups of all types in PEi-*g*-PA12 samples with different concentrations of PEi before the synthesis of these products.

This method can be conveniently used for other linear and branched polyamides that consist of different amino groups.

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