

Anionic Polymerization of Lactams: A Comparative Study on Various Methods of Measuring the Conversion of ϵ -Caprolactam to Polyamide 6

Cai-Liang Zhang,¹ Lian-Fang Feng,^{1,2} Guo-Hua Hu^{2,3}

¹State Key Laboratory of Polymer Reaction Engineering, College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, China

²Laboratory of Chemical Engineering Sciences, CNRS-ENSIC-INPL, 1 rue Grandville BP 20451, 54001 Nancy, France

³Institut Universitaire de France, Maison des Universités, 103 Boulevard Saint-Michel, 75005 Paris, France

Received 15 August 2005; accepted 3 November 2005

DOI 10.1002/app.23659

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Anionic ring-opening polymerization of lactams leads to the formation of poly(lactams) or polyamides. This work aimed at comparing the performance of four methods for measuring the conversion of ϵ -caprolactam (CL) to polyamide 6. The latter was either a homopolymer (PA6) or grafts onto polystyrene (PS-g-PA6 graft copolymer). Those four methods were mass balance based on solvent extraction (methanol, water, THF, or acetone), mass balance based on vacuum drying at 140°C, thermogravimetric analysis (TGA), and elemental analysis based on nitrogen. The mass balances based on methanol extraction and

vacuum drying at 140°C and TGA were all suitable for measuring the conversion of CL, whether the resulting polymer was the PA6 or PS-g-PA6. The mass balance based on water extraction was good for the PA6 and not good for the PS-g-PA6. The elemental analysis based on nitrogen was not suitable for the PA6 nor for the PS-g-PA6. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1972–1981, 2006

Key words: anionic polymerization; poly(lactams); reactive extrusion; reactive processing; thermogravimetric analysis

INTRODUCTION

The conversion of lactams to poly(lactams), also called polyamides, by anionic ring-opening polymerization has been studied very extensively. Among the various lactams, ϵ -caprolactam (CL) is by far the most studied one. The final product can be a homopolymer—polyamide 6 (PA6),^{1–4} a more or less random copolymer of CL and another lactam,^{5–7} a pure block/graft copolymer with PA6 as block(s) or graft(s),^{8–12} or a blend composed of PA6 and other polymers.^{13–17}

Various methods have been proposed to determine the conversion of CL. They include gravimetry,^{3,12,13,18–27} gas chromatography,^{28,29} enthalpy of polymerization,^{4,30} and in-line infrared spectroscopy.³¹ Among them, the gravimetry is used the most. It is based on the ratio of the mass of the polymerized product whose residual monomer is removed over its

initial mass. The performance of this type of method depends very much on how easy and the extent to which the residual monomer is removed. The residual monomer can be removed in different ways. For example, polymerized products are first cut and grinded. The residual monomer is then extracted with freshly distilled water,^{18–20} methanol,^{3,21–27} or acetone.¹³ Another way is to remove the residual monomer under vacuum and at high temperatures.³² To the authors' knowledge, thermogravimetric analysis (TGA) has not yet been used for determining the monomer conversion. However, it could be a suitable method because it is also based on mass balance and follows the instantaneous mass loss of a product as temperature increases and has been mostly used for studying the thermal degradation of polymers.^{33,34}

This work aimed at comparing a few analytical methods for determining the conversion of CL to PA6 for two different polymerizing systems. The analytical methods were gravimetry by solvent extraction, vacuum drying at 140°C, TGA, and elemental analysis based on nitrogen. As for the two polymerizing systems, one was the anionic homopolymerization of CL and contained CL, sodium ϵ -caprolactam (NaCL), and a small isocyanate compound—micro-activator. The final product was expected to be a homopolyamide 6 and will be denoted as PA6. The other one was the grafting polymerization of CL onto an isocyanate

Correspondence to: G.-H. Hu (hu@ensic.inpl-nancy.fr).

Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50390097, 20310285.

Contract grant sponsor: AFRST (Association Franco-Chinoise pour la Recherche Scientifique et Technique); contract grant number: PRA Mx02–07.

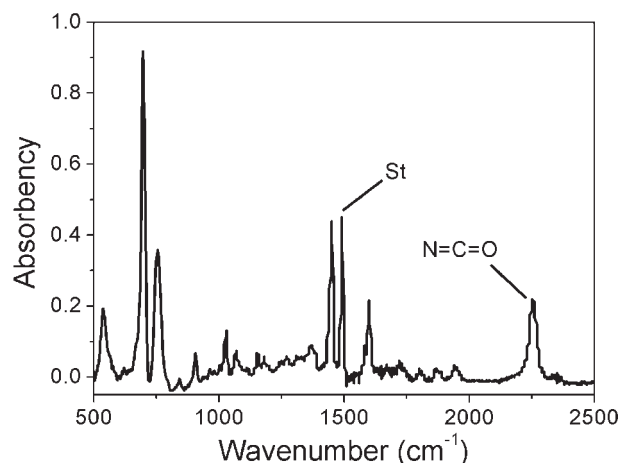


Figure 1 FTIR spectrum of the PS-*co*-TMI.

bearing polystyrene backbone and contained CL, NaCL, and a random copolymer of styrene and 3-isopropenyl- α , α -dimethylbenzene isocyanate (TMI). The latter was a macro-activator and will be denoted as PS-*co*-TMI. The final product was expected to be a graft copolymer with PS as the backbone and PA6 as grafts and will be designated as PS-g-PA6.

EXPERIMENTAL

Materials

The two monomers used for synthesizing PS-*co*-TMI, styrene (St), and TMI were purchased from Aldrich. Before use, the St was purified over an aluminum oxide column and the TMI was not subjected to any purification. The latter had a formula mass of 201.27 g/mol. Its boiling temperature was about 270°C/760 mmHg. Benzoyl peroxide (BPO) was used as the free radical initiator. It was purified by dissolution in methanol, precipitation in chloroform, and was then dried in a vacuum oven at room temperature. Toluene was used as the solvent for the copolymerization and was purified by boiling in the presence of anhydrous calcium oxide. CL was purified by rectification under vacuum. Its melting temperature was 69~71°C and its boiling temperature was 268.5°C/760 mmHg and 139°C/12 mmHg, respectively. The catalyst used for

the anionic polymerization was supplied by DSM in the form of a mixture of NaCL and CL containing 1.4 mol NaCL/kg CL. It will be denoted as Cat. The micro-activator was 2,4-tolunene diisocyanate (TDI) with a formula mass of 174.16 g/mol.

Synthesis of PS-*co*-TMI

The PS-*co*-TMI was prepared by solution polymerization using a one liter glass reactor equipped with a mechanical agitator. The composition of the St/TMI/BPO/toluene polymerization system was 60 mL/1.6 mL/0.2 g/40 mL. Toluene was first charged to the reactor followed by St, TMI, and BPO. The reactor was purged by nitrogen and its temperature was controlled at 80°C by circulating water. The polymerization process lasted 24 h. The product thus obtained was precipitated twice in methanol, filtered, and then vacuum-dried at 80°C for 24 h.

The number and mass average molar masses of the PS-*co*-TMI measured by size exclusion chromatography were 33.3 and 97.0 kg/mol, respectively. Its TMI content was measured by a method reported in the literature³⁵ and was found to be 4 wt %. Figure 1 shows its infrared spectrum. It was characterized by a peak at 2255 cm⁻¹ corresponding to the isocyanate group of the TMI and by another one at 1492 cm⁻¹ corresponding to St.

Synthesis of PS-g-PA6 graft copolymer and homopolymer PA6

A Haake torque rheometer was used for the anionic polymerization of CL. It had a volume capacity of about 60 mL and was equipped with two screws. During the polymerization, the latter rotated in the opposite directions to ensure mixing. Before the polymerization, CL, Cat, and PS-*co*-TMI macro-activator (or TDI micro-activator) were first mixed in a beaker and then charged to the mixing chamber of the Haake torque rheometer that was preheated to 230°C. Samples were taken from the mixing chamber after prescribed mixing times. Table I gathers some information on the experimental trials carried out in this work. The molar masses of the resulting PS-g-PA6 graft co-

TABLE I
Selected Information on the Experimental Trials Carried Out in This Work

Exp.	Mass composition	Polymerization temperature (°C)	Reaction time (min)
E1	PS- <i>co</i> -TMI/CL/Cat = 18/42/3	230	8
E2	PS- <i>co</i> -TMI/CL/Cat = 30/30/3	230	8
E3	PS- <i>co</i> -TMI/CL/Cat = 42/18/3	230	8
E4	PS- <i>co</i> -TMI/CL/Cat = 30/30/1	230	14
E5	TDI/CL/Cat = 1.8/50/3	230	6

polymers were not measured because of the lack of an appropriate solvent capable of dissolving them. However, they can be easily estimated based on the following equation^{12,36}:

$$\frac{M_{\text{PS-g-PA6}}}{M_{\text{PS-co-TMI}}} = 1 + \frac{(W_{\text{CL},0} + W_{\text{Cat},0} \times 97.4\%)p}{W_{\text{PS-co-TMI}}} \quad (1)$$

where $M_{\text{PS-co-TMI}}$ and $M_{\text{PS-g-PA6}}$ are the molar masses of the PS-co-TMI and the resulting PS-g-PA6 graft copolymer, respectively; $W_{\text{PS-co-TMI}}$, $W_{\text{CL},0}$, and $W_{\text{Cat},0}$ are the initial masses of the PS-co-TMI, CL, and Cat, respectively; and 97.4% is the mass percentage of the equivalent CL in the Cat. Considering the compositions used and the CL conversion values obtained in this work, the molar masses of the PS-g-PA6 would be ~1.5–3.5 times that of the PS-g-TMI. In other words, the number-average molar masses of the PS-g-PA6 would quite likely range from 50 to 120 kg/mol and the mass-average molar masses from 145 to 340 kg/mol.

Methods used for the determination of the CL conversion

Prior to the determination of the conversion of CL to the PS-g-PA6 graft copolymer or PA6 homopolymer, samples were all subjected to the following pretreatment. They were pressed with a hot press at 200°C and 30 MPa to films of about 200 μm thick. The whole process took about 3 min. The films were then dried under vacuum at 50°C for 12 h to remove traces of water. The importance of this predrying procedure will be discussed later. The amounts of the CL remained in the films were subsequently measured by the following methods.

Method 1: Gravimetry by solvent extraction

Known amounts (about 0.5 g) of predried films were placed in one of the following solvents under reflux (water, methanol, THF, or acetone) for 1 h to extract the residual monomer from the films. This duration was found to be largely enough for water or methanol. The extracted films were then vacuum-dried at 80°C for 12–48 h. Finally their masses were weighted. The CL conversion was calculated using the following equation:

$$\text{CL}\% = \left[1 - \frac{W_1 - W_2}{W_1 \times (W_{\text{CL},0} + W_{\text{Cat},0} \times 97.4\%)/W} \right] 100\% \quad (2)$$

where W_1 and W_2 are the masses of the polymerized product before and after extraction, respectively; W is the initial total mass of the polymerizing system.

Method 2: Vacuum drying at 140°C

Known amounts (about 0.5 g) of predried films were placed in a vacuum oven at 140°C for 24 h. The mass losses were considered to be the amounts of CL that remained in the films before the vacuum drying. The CL conversion was calculated using the following equation:

$$\text{CL}\% = \left[1 - \frac{W_3 - W_4}{W_3 \times (W_{\text{CL},0} + W_{\text{Cat},0} \times 97.4\%)/W} \right] 100\% \quad (3)$$

where W_3 and W_4 are the masses of the polymerized product before and after vacuum drying at 140°C.

Method 3: TGA

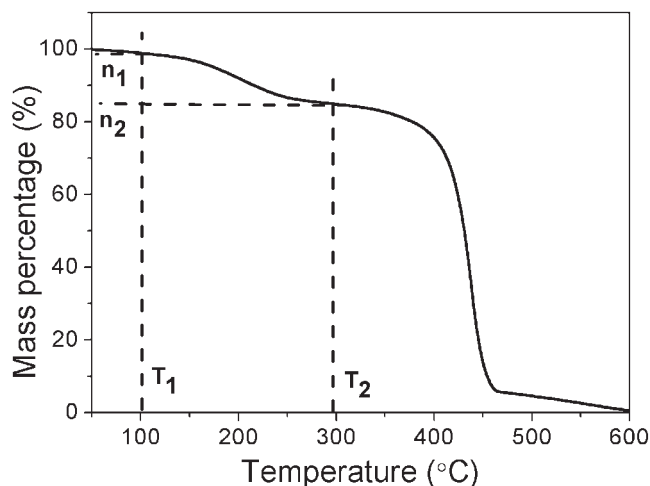
A TGA of type Perkin-Elmer, Pyris 1, was used. Its accuracy was within 0.1 μg. Predried films (about 2 mg) were heated from 25 to 600°C at 10°C/min under nitrogen. A typical TGA diagram is shown in Figure 2(a). Its differential form is shown in Figure 2(b). It is seen that the mass loss took place most significantly in two different temperature ranges. The first one was between 100 and 300°C and was a result of small molecule evaporation. The second one was located between 350 and 465°C and corresponded to the thermal degradation of the polymer product. The first mass loss was actually due to the evaporation of CL, since its melting and boiling temperatures were 69–71 and 268.5°C/760 mmHg, respectively. Figure 2(b) shows that the CL started to evaporate at about 100°C (T_1) and the evaporation was complete at about 300°C (T_2). The CL conversion was calculated according to the following equation:

$$\text{CL}\% = \left[1 - \frac{n_1 - n_2}{(W_{\text{CL},0} + W_{\text{Cat},0} \times 97.4\%)/W} \right] 100\% \quad (4)$$

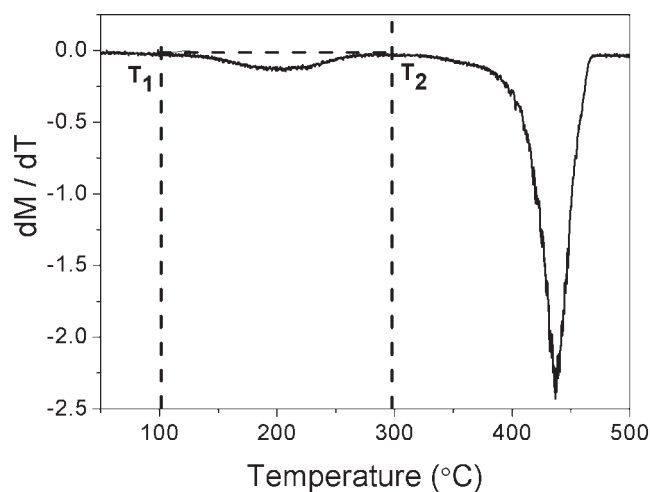
where n_1 and n_2 are the mass percentages of the product at the beginning and at the end of the evaporation of CL.

Method 4: Elemental analysis

Predried films were first put in boiling methanol for 1 h to extract the residual CL from them and then dried in a vacuum oven at 80°C for 12 h. They were finally stored in a desiccator. The nitrogen contents of the films before and after extraction in boiling methanol were measured by element analysis. The CL conversion was calculated by the following equation:



(a)



(b)

Figure 2 TGA diagrams of a typical product obtained by the anionic grafting polymerization of CL onto PS-co-TMI. (a) Accumulated mass loss as a function of temperature increase; (b) instantaneous mass loss as a function of temperature increase.

$$\text{CL}\% = \left[\frac{N_2 - N_3 \times 7\%}{N_1 - N_3 \times 7\%} \right] 100\% \quad (5)$$

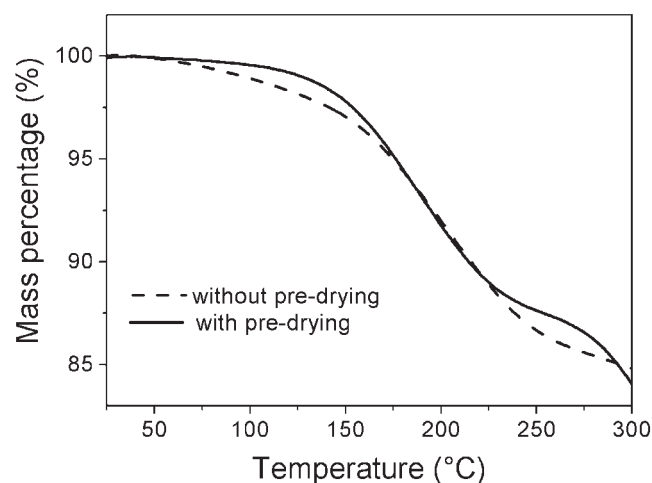
where N_1 and N_2 are the nitrogen contents in the polymerized product before and after extraction in methanol, respectively; N_3 is the TMI mass content in PS-co-TMI (%); 7% is the nitrogen content in TMI.

RESULTS AND DISCUSSION

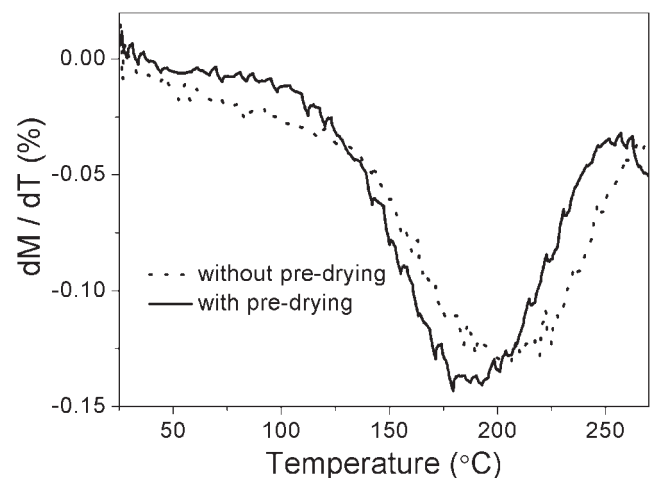
Importance of the predrying of polymerized product films

Polymerized products were expected to contain PS-g-PA6 graft copolymer (or PA6 homopolymer) and CL residue. They were all prone to water absorption,

especially the latter. Thus removal of the absorbed water seemed to be necessary for the subsequent determination of the CL conversion. This was confirmed by the TGA traces (Fig. 3) of the polymerized product E4 with and without predrying in a vacuum oven at 50°C for 12 h. Without predrying, the films started to lose mass at about 50°C. With the predrying, the mass loss was noticeable only at about 100°C. These results confirmed that water started to evaporate at a much lower temperature than CL, as expected. When the temperature reached about 260°C, the rate of the mass loss was significantly reduced. This implies that at that temperature both water and CL residue were completely removed. It is interesting to note that the difference in mass between the two films (one with the predrying and the other one without predrying) at



(a)



(b)

Figure 3 Effect of the predrying in a vacuum oven at 50°C for 12 h on the TGA diagrams of the polymerized product of the experiment E4. (a) Accumulated mass loss as a function of temperature increase; (b) instantaneous mass loss as a function of temperature increase.

TABLE II
Mass Losses of Various Polymerized Products Subjected to Different Predrying Times in a Vacuum Oven at 50°C

Exp.	CL content in the polymerizing system (%)	Masses at different predrying times (g)			Mass loss percentage (%) ^a
		0 h	12 h	24 h	
E1	69.7	0.5358	0.5301	0.5301	2.38
E2	51.6	0.5108	0.5020	0.5016	1.80
E4	50.6	0.5245	0.5147	0.5147	1.87
E3	32.6	0.5378	0.5250	0.5243	1.06

^aCalculated based on the masses after 12 h predrying.

100°C was the same as that at 260°C. Moreover, that mass difference was also very similar to that obtained by the predrying procedure. Those results confirm that mass difference was indeed related to the amount of water absorbed in the films. Table II shows the mass losses of various polymerized products after different predrying times. It is seen that 12 h was long enough to remove the absorbed water. Moreover, the higher the CL mass percentage in the polymerizing system, the higher the water content in the film, as expected.

Performances of the various methods of measuring the CL conversion for grafting polymerization system

Method 1: Gravimetry by solvent extraction

Table III shows the CL conversions obtained by extraction in different solvents followed by vacuum drying at 80°C for 24 h. It is noted that while the measured CL conversions followed the order THF < acetone < methanol < water for the experiments E2 and E3, those for the experiment E1 almost followed the opposite order: THF > acetone > methanol > water.

This might be explained by one of the following two different scenarios. The first one is that the PS-g-PA6 graft copolymer might contain molecules with very short PA6 grafts. Their solubility characteristics could be very similar to those of the PS-co-TMI. The second one is that all PS-co-TMI chains might not have been able to participate in the anionic grafting polymerization. Unlike water or methanol, when acetone or THF was used as a solvent, those two types of chains could be extracted from the polymerized products. As a result, the measured CL conversion values could be

TABLE III
Comparison of the CL Conversions Measured by Extraction in Various Solvents

The product of experiment	CL conversion obtained by extraction (%)			
	Water	Methanol	Acetone	THF
E1	93.7	87.7	95.5	95.8
E2	95.8	90.9	86.0	71.0
E3	95.9	93.2	82.3	79.9

lower than the cases where water or methanol was used as the solvent. To verify those hypotheses, the following experiment was done (Fig. 4). The polymerized product E2 was first extracted in methanol under reflux for 1 h. The insoluble material (solute A) was vacuum-dried at 80°C for 24 h and then extracted in THF under reflux for 1 h. The resulting solution (solution D) was subjected to evaporation. The final residue E was analyzed by FTIR, ¹³C-NMR, and UV, respectively. As shown in Figure 5, the FTIR spectra of PS-co-TMI and the residue E were basically the same except that the former had a peak at 2255 cm⁻¹ characteristic of the isocyanate group of the TMI, and the latter did not have it but had a new peak at 1641 cm⁻¹ characteristic of PA6. This implies that all TMI moieties in the PS-co-TMI chains had participated in the anionic polymerization of CL. Also the FTIR spectrum of the product (PS-co-TMI-CL) resulting from a reaction of the PS-co-TMI with an excess of CL alone was

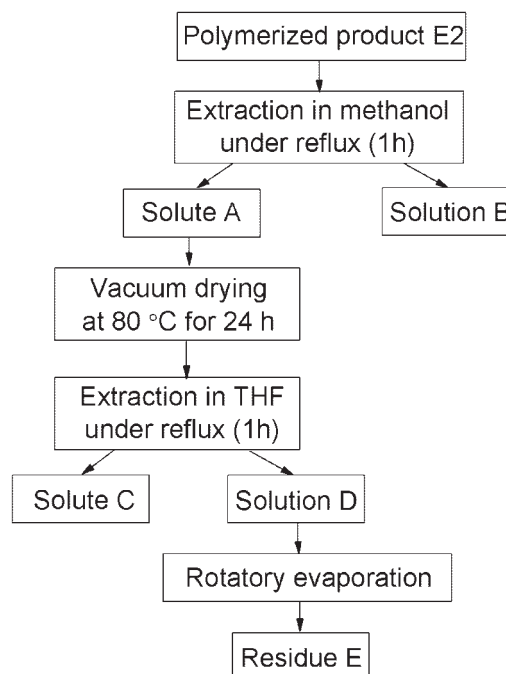


Figure 4 Procedure used for preparing a sample for FTIR, ¹³C-NMR, and UV analyses.

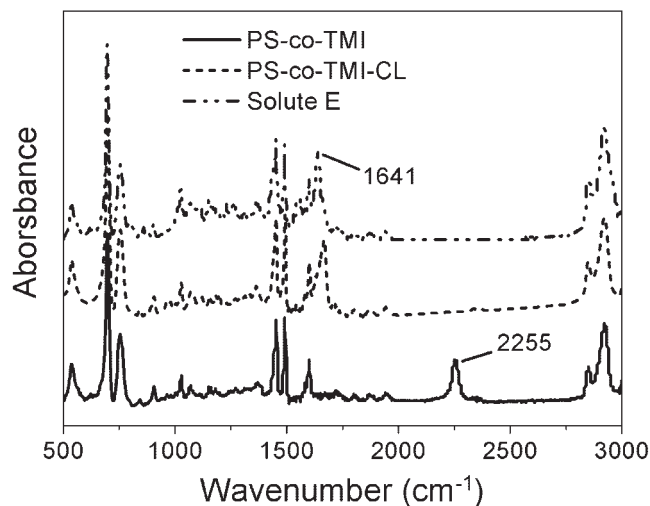


Figure 5 FTIR spectra of (1) the PS-co-TMI, (2) the PS-co-TMI-CL, and (3) residue E.

similar with that of residue E. Those results indicate that residue E was not PS-co-TMI but PS-co-TMI-CL or PS-g-PA6 chains whose PA6 grafts were short enough to be soluble in THF. This conclusion was further supported by the ^{13}C -NMR spectra in Figure 6. New

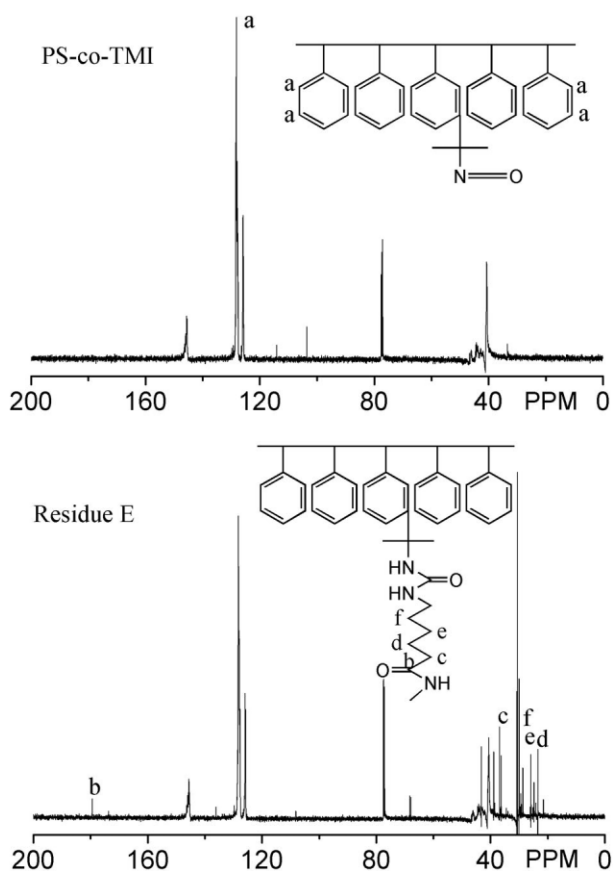


Figure 6 ^{13}C -NMR spectra of (1) the PS-co-TMI and (2) residue E. Those spectra were obtained in CDCl_3 .

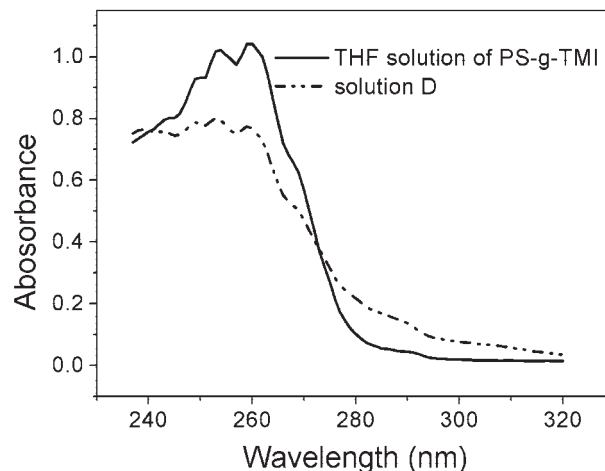


Figure 7 UV spectra of (1) PS-co-TMI in THF and (2) solution D.

peaks corresponding to the PA6 appeared in residue E.

Figure 7 compares the UV spectrum of the PS-co-TMI in THF with that of solution D. Both had a peak at 259 nm characteristic of styrene. Nevertheless, they differed to a certain degree, suggesting that residue E was not the PS-co-TMI but likely PS-g-PA6 graft copolymer with very short PA6 grafts.

As shown in Table III, the CL conversions from the methanol extraction were lower than those from the water extraction. A question then arose of which one to use. To answer it, the following experiment was done (Fig. 8). The polymerized product E2 was first extracted in water under reflux for 1 h. The resulting solute (F) was then vacuum-dried at 80°C for 24 h. A known amount (0.5032 g) of the dried solute was further extracted in boiling methanol for 1 h. After vacuum drying at 80°C for 24 h, its mass became

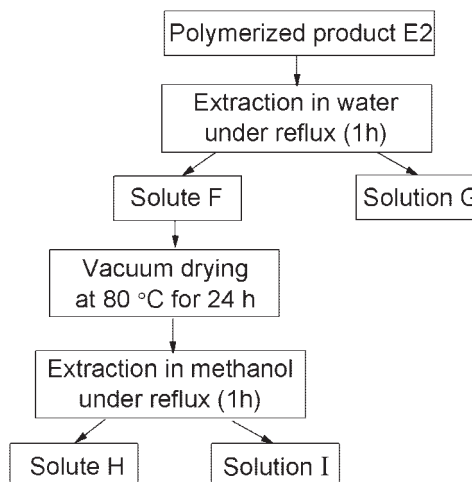


Figure 8 Procedure used for evaluating the performance of water and methanol as solvent for extraction.

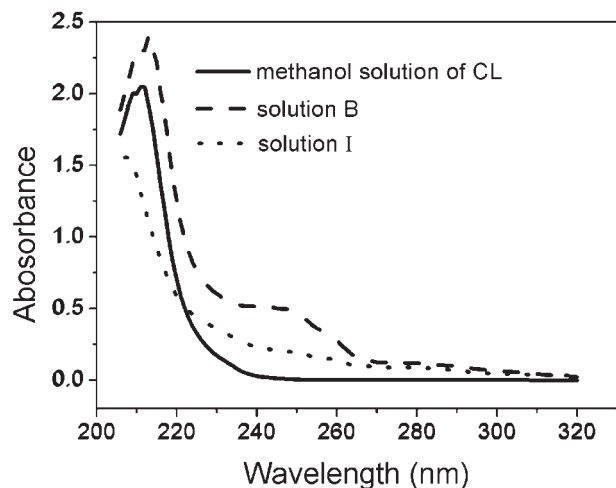


Figure 9 UV spectra of (1) the solution of CL, (2) solution B, and (3) solution I.

0.4932 g. In other words, there was 0.01 g decrease in mass after the methanol extraction.

Figure 9 compares the UV spectra of three products: (a) the methanol solution of CL, (b) solution B, and (c) solution I. They all had a peak at about 212 nm characteristic of CL. This suggests that water alone was unable to completely extract the CL residue from the polymerized product because further CL was extracted during the subsequent extraction with methanol. Therefore, methanol was better capable of extracting the CL residue from the polymerized product than water. Based on the respective mass decreases as a result of the water and methanol extraction steps, the CL conversion was recalculated to be 92.0%, which was much closer to that obtained from the methanol extraction (90.9%).

Table IV shows the minimum time necessary for the polymerized product E2 extracted in various solvents to reach a constant mass under vacuum drying at 80°C. While 12 h was enough for water or methanol, 36 h was needed for acetone or THF. Acetone and THF were good solvents of the PS part of the PS-*g*-PA6 graft copolymer. As such, longer times were needed for them to get out from the copolymer. On the other

TABLE IV
Times Necessary for Complete Solvent Removal Under Vacuum Drying at 80°C

Solvents extraction for product of experiment E2	Mass percentages after various drying times (%)			
	12 h	24 h	36 h	48 h
Water extraction	97.9	97.8	97.8	—
Methanol extraction	95.3	95.2	95.2	—
THF extraction	86.2	85.2	85.0	84.8
Acetone extraction	93.6	93.1	92.9	92.7

TABLE V
CL Conversions Measured by Vacuum Drying at 140°C for 24 h

Polymerized product	CL conversion (%)
E1	87.3
E2	90.0
E3	92.3

hand, water and methanol were good solvents neither for the PS part of the graft copolymer nor for its PA6 part. Thus they could be removed completely in a much shorter period of time. From this viewpoint, methanol and water were also more efficient solvents for CL extraction than acetone and THF.

The results above suggest that a good solvent for extracting CL from a polymerized product like E2 should be one which should not have too strong or too weak affinity with either of the two parts of the PS-*g*-PA6 graft copolymer. Methanol seems to be the best compromise of the four solvents tested (methanol, water, THF, and acetone).

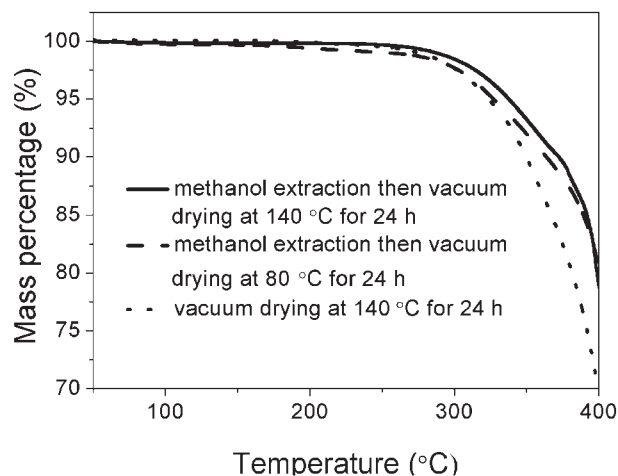
Method 2: Vacuum drying at 140°C for 24 h

The performance of this method depends very much on how easy and the extent to which the CL residue is removed from polymerized products. To confirm that the CL residue was indeed removed thoroughly by vacuum drying at 140°C, the polymerized product E2, which had already been vacuum-dried at 140°C for 24 h, was placed in boiling methanol and was kept there for 1 h. It was then vacuum-dried at 80°C for 24 h. It was found that its mass after the methanol extraction basically did not change with respect to its mass before the extraction, indicating that vacuum drying at 140°C for 24 h was enough to completely remove the CL residue from the polymerized product.

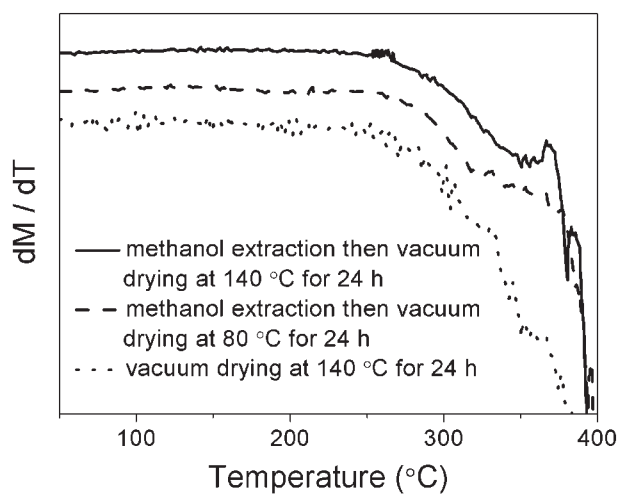
Table V shows the CL conversion of the experiments E1–E3 measured by vacuum drying at 140°C for 24 h. Comparison of the data in this table with those obtained by methanol extraction followed by vacuum drying at 80°C for 24 h in Table III shows that they were almost the same, further confirming the conclusion that both the vacuum drying at 140°C for 24 h and methanol extraction followed by vacuum drying at 80°C for 24 h were good methods for determining the CL conversion of the PS-*co*-TMI/CL/NaCl anionic polymerization system.

Method 3: TGA

TGA is based on mass balance and follows the instantaneous mass loss of a product as temperature increases. Therefore, it can also be a good method to verify whether or not there are small molecules in



(a)



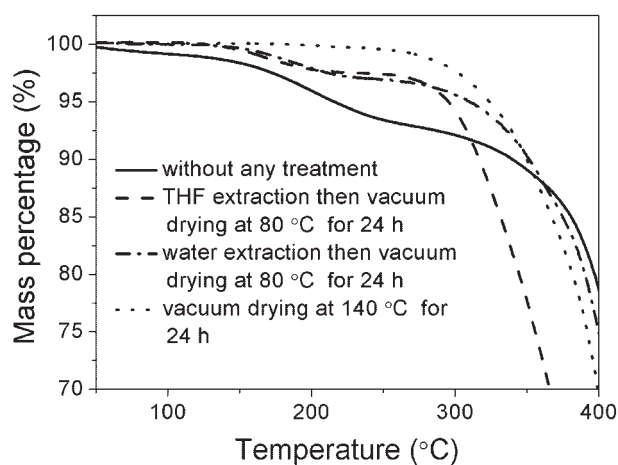
(b)

Figure 10 TGA traces of the polymerized product E2 subjected to one of the following treatments: (1) methanol extraction then vacuum drying at 140°C for 24 h, (2) methanol extraction then vacuum drying at 80°C for 24 h, and (3) vacuum drying at 140°C for 24 h. (a) Remaining mass percentage and (b) instantaneous loss in the mass percentage.

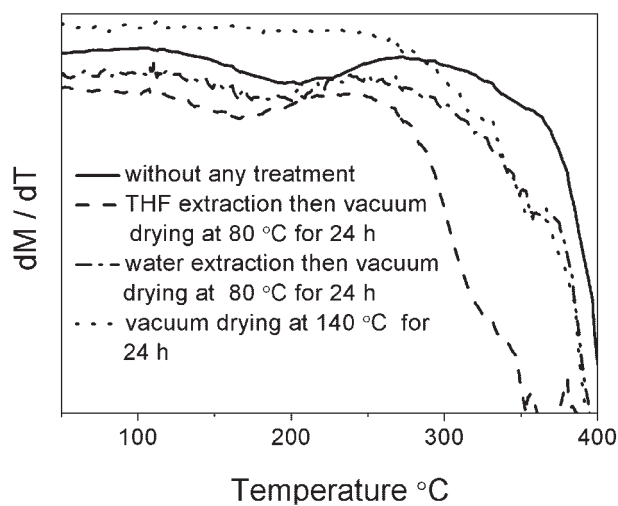
polymers. Figure 10 shows the TGA traces of the polymerized product E2, which was subjected to one of the three different treatments beforehand: (1) methanol extraction and then vacuum drying at 140°C for 24 h; (2) methanol extraction and then vacuum drying at 80°C for 24 h; and (3) vacuum drying at 140°C for 24 h. It is seen that in all cases, the mass of the polymerized product E2 started to decrease only after 260°C. This is another confirmation that the removal of the CL residue was indeed complete in all those three cases.

Figure 11 shows the TGA traces of the polymerized product E2, which was subjected to (1) no treatment; (2) THF extraction and then vacuum drying at 80°C for 24 h; (3) water extraction and then vacuum drying at 80°C for 24 h; and (4) vacuum drying at 140°C for 24 h.

at 80°C for 24 h; or (4) vacuum drying at 140°C for 24 h. It is seen that unlike the methanol extraction followed by vacuum drying at 80°C for 24 h or the vacuum drying at 140°C for 24 h, the polymerized product E2 treated by the water or THF extraction followed by vacuum drying at 80°C for 24 h still lost its mass in the temperature range between 120 and 260°C. This indicates that either the CL residue or water (THF) or both were not completely removed. Those results were consistent with the aforementioned ones. The CL conversion could easily be determined from the TGA trace of the product without having been subjected to any treatment. The only difficulty was to fix up a temperature at which the CL residue could be considered being completely removed. It



(a)



(b)

Figure 11 TGA traces of the polymerized product E2 subjected to (1) no treatment, (2) THF extraction and then vacuum drying at 80°C for 24 h, (3) water extraction and then vacuum drying at 80°C for 24 h, and (4) vacuum drying at 140°C for 24 h. (a) Remaining mass percentage and (b) instantaneous loss in the mass percentage.

TABLE VI
CL Conversions Obtained by the Nitrogen Analysis

Experiment	CL conversion (%)
E1	89.0
E2	97.6
E3	98.0
E4	94.3

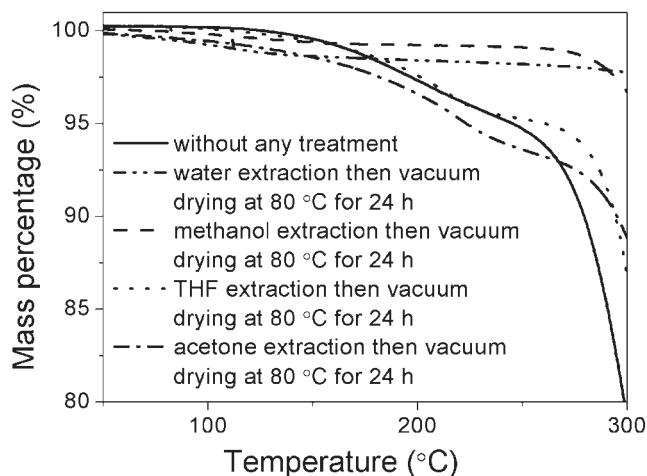
could be somewhere between 260 and 270°C. The corresponding conversion would then be somewhere between 90.3 and 89.8. That value was close enough to that obtained by methanol extraction or vacuum drying at 140°C for 24 h. Thus, TGA could also be a suitable method for measuring the CL conversion.

Method 4: Elemental analysis

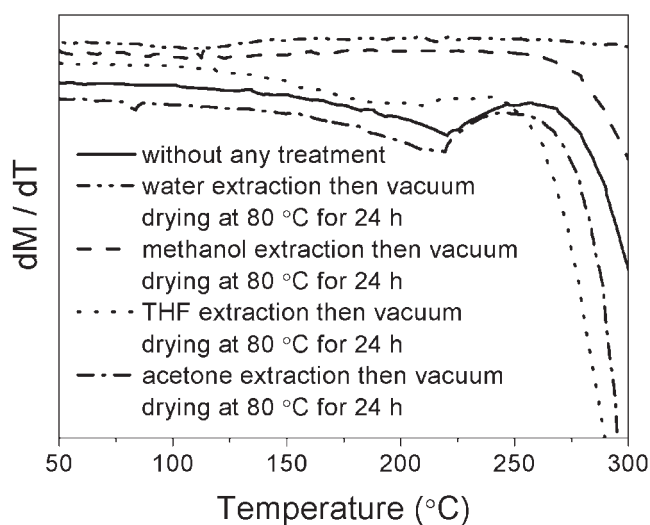
Polymerized products contained nitrogen. The latter came from the PS-g-TMI, CL, and Cat. Thus, in principle it was possible to determine the CL conversion by nitrogen analysis. Table VI shows the CL conversion values for the experiments E1–E4. They were much higher than those obtained by methanol extraction followed by vacuum drying at 80°C for 24 h (Table III), vacuum drying at 140°C for 24 h (Table V), and TGA. Thus, the nitrogen method was not suitable for measuring the CL conversion of the grafting anionic polymerization system. The reason remains unclear.

Suitability of the above methods for the anionic homopolymerization system

Table VII compares the CL conversions of the polymerized product E5 obtained by extraction in various solvents followed by vacuum drying at 80°C for 36 h. From Table VII, it may be seen that the conversions of CL to PA6 by extraction in water and methanol were much lower than those by extraction in THF and acetone. To assess which solvents were suitable, the samples of the polymerized product E5 after extraction in those solvents were analyzed by the TGA. As shown in Figure 12, there was basically no mass loss till 260°C for the sample subjected to extraction in



(a)



(b)

Figure 12 TGA traces of the polymerized product E5 subjected to one of the following treatments: (1) without any treatment, (2) water extraction then vacuum drying at 80°C for 24 h, (3) methanol extraction then vacuum drying at 80°C for 24 h, (4) THF extraction then vacuum drying at 80°C for 24 h, and (5) acetone extraction then vacuum drying at 80°C for 24 h. (a) Accumulated mass loss and (b) instantaneous mass loss.

TABLE VII
CL Conversions Measured by Extraction in Various Solvents

Solvent used for extraction of E5	Mass percentages after various times of vacuum drying (g)				CL conversion (%) ^a
	0 h	12 h	24 h	36 h	
Water	0.5312	0.4817	0.4782	0.4786	89.7
Methanol	0.4910	0.4464	0.4442	0.4437	90.0
THF	0.4940	0.4882	0.4845	0.4843	98.0
Acetone	0.5380	0.5265	0.5216	0.5213	96.8

^aThe conversions were calculated based on 36 h.

TABLE VIII
CL Conversions of E5 Obtained by Vacuum Drying at 140°C and TGA

Measuring method	CL conversion (%)
Vacuum drying at 140°C	89.7
TGA	90.5

methanol or water. This indicates that small molecules were successfully and thoroughly removed from the polymerized product during the extraction in methanol or water. On the other hand, the sample extracted in THF or acetone started to lose mass at a relatively low temperature, say 120°C. This implies that THF or acetone was unable to remove the small molecules from the polymerized product in a thorough manner.

Table VIII shows the CL conversions of the polymerized product E5 measured by the vacuum drying at 140°C for 24 h and TGA, respectively. Inspection of Tables VII and VIII shows that the vacuum drying at 140°C for 24 h, the TGA, and the extraction in methanol or water all yield very similar values for the CL conversion. Those results suggest that they were all good for measuring the conversion of the anionic homopolymerization of CL.

CONCLUSIONS

In this work, the performance of four methods for measuring the conversion of ϵ -caprolactam (CL) to polyamide 6 by activated anionic polymerization was compared. The resulting polyamide was either a homopolymer (PA6) or grafted onto polystyrene (PS-*g*-PA6 graft copolymer). Those four methods were mass balance based on solvent extraction (methanol, water, THF, or acetone), mass balance based on vacuum drying at 140°C, thermogravimetric analysis (TGA), and elemental analysis based on nitrogen. The mass balances based on methanol extraction and vacuum drying at 140°C and TGA were all suitable for measuring the conversion of CL, whether the resulting polymer was the PA6 or PS-*g*-PA6. The mass balance based on water extraction was good for the PA6 and not good for the PS-*g*-PA6. The one based on THF or acetone extraction was neither good for the PA6 system nor for the PS-*g*-PA6 one. The elemental analysis based on nitrogen was not suitable for them either.

References

- Šebenda, J. In *Comprehensive Polymer Science*; Allen, S. G.; Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Vol. 3, p 521.
- Šebenda, J. *J Macromol Sci Chem* 1972, 6, 1145.
- Udipi, K.; Davé, R. S.; Kruse, R. L.; Stebbins, L. R. *Polymer* 1997, 38, 927.
- Davé, R. S.; Kruse, R. L.; Stebbins, L. R.; Udipi, K. *Polymer* 1997, 38, 939.
- Šebenda, J. In *Lactam-Based Polyamides*; Puffr, R.; Kubanek, V., Eds.; CRC Press: Florida, 1991; Vol. 1, p 29.
- Byong, J. K.; White, J. L. *J Appl Polym Sci* 2003, 88, 1429.
- Ha, S. K.; White, J. L. *Int Polym Process* 1998, 13, 136.
- Harrats, C.; Fayt, R.; Jérôme, R. *Polymer* 2002, 43, 5347.
- Yuya, Y.; Hisashi, M.; Koichi, I. *J Polym Sci Polym Chem Ed* 1972, 10, 3577.
- Fayt, R.; Jérôme, R.; Teyssié, Ph. *J Polym Sci Part A: Polym Chem* 1989, 27, 2823.
- Petit, D.; Jérôme, R.; Teyssié, Ph. *J Polym Sci Polym Chem Ed* 1979, 17, 2903.
- Hu, G. H.; Li, H.; Feng, L. F. *Polymer* 2005, 46, 4562.
- Hu, G. H.; Cartier, H.; Plummer, C. *Macromolecules* 1999, 32, 4713.
- Cartier, H.; Hu, G. H. *Polymer* 2001, 42, 8807.
- Hu, G. H.; Li, H.; Feng, L. F. *Macromolecules* 2002, 35, 8247.
- Hu, G. H.; Cartier, H.; Feng, L. F.; Li, B. G. *J Appl Polym Sci* 2004, 91, 1498.
- Hu, G. H.; Li, H.; Feng, L. F.; Pessan, L. A. *J Appl Polym Sci* 2003, 88, 1799.
- Warakomski, J. M. *Chem Mater* 1992, 4, 1000.
- Marelová, J.; Roda, J.; Stehlíček, J. *Eur Polym J* 1999, 35, 145.
- Dai, L. X.; Huang, N. X.; Tang, Z. L.; Hungenberg, K. D. *J Appl Polym Sci* 2001, 82, 3184.
- Yn, M. S.; Ma, C. C. M.; Lin, S. H.; Wu, Y. D. *Compos Sci Technol* 1995, 54, 123.
- Mateva, R.; Ishtinakova, O.; Nikolov, R. N.; Djambova, Ch. *Eur Polym J* 1998, 34, 1061.
- Mateva, R.; Petrov, P. *Eur Polym J* 1999, 35, 325.
- Ricco, L.; Russo, S. *Macromolecules* 1999, 32, 7726.
- Mateva, R.; Petrov, P.; Rousseva, S.; Dimitrov, R.; Zolova, G. *Eur Polym J* 2000, 36, 813.
- Rusu, G.; Ueda, K.; Rusu, E.; Rusu, M. *Polymer* 2001, 42, 5669.
- Hu, Y. H.; Chen, C. Y.; Wang, C. C.; Huang, Y. H.; Wang, S. P. *J Polym Sci Part A: Polym Chem* 2004, 42, 4976.
- Ongemach, G. C.; Moody, A. C. *Anal Chem* 1967, 39, 1005.
- Francesco, Z. G.; Giovanni, M. S.; Paolo, C. *Anal Chem* 1969, 41, 1847.
- Kotelnikov, V. A.; Persits, I. E.; Surin, N. N.; Danilevskaya, L. B.; Sekiguchi, H.; Bui, C. *Eur Polym J* 1996, 32, 767.
- Haberstroh, E.; Jakisch, L.; Henßge, E.; Schwarz, P. *Macromol Mater Eng* 2002, 287, 203.
- Aelion, R. *Ind Eng Chem* 1961, 53, 826.
- Draye, A. C.; Persenaire, O.; Broek, J.; Roda, J.; Košek, T.; Dubois, P. *Polymer* 2001, 42, 8325.
- Bettini, S. H. P.; Agnelli, J. A. M. *Polym Test* 2000, 19, 3.
- Li, G. Z.; Feng, L. F.; Gu, X. P.; Xu, Z. B.; Hu, G. H.; Liu, J. H. *J Funct Polym* 2005, 18, 127.
- Hu, G. H.; Li, H.; Feng, L. F. *J Appl Polym Sci*, in press.