ELSEVIER

Polymer 41 (2000) 3555–3560

polymer

Polyamides incorporating furan moieties
3. Polycondensation of 2-furamide with paraformaldehyde

M. Abid[a], R. El Gharbi[a], A. Gandini[b,*]

[a]*Laboratoire de Synthèse et Physicochimie Organique, Faculté des Sciences, Université de Sfax, 3038 Sfax, Tunisia*
[b]*Matériaux Polymères, Ecole Française de Papeterie et des Industries Graphiques (INPG), BP65, 38402 Saint Martin d'Hères, France*

Received 1 June 1999; accepted 4 August 1999

Abstract

2-Furamide was treated with an excess of paraformaldehyde in an acidic medium to promote both its oxymethylation and the subsequent polycondensation of the reaction product involving the C5 position of the heterocycle. The molecular weight of ensuing 2,5-furanmethylene polyamide was optimised by examining the role of the synthetic procedure, the catalyst and medium used and the reaction temperature.

Keywords: Paraformaldehyde; Polycondensation; Oxymethylation

1. Introduction

This study is a contribution to the field of polymers bearing furan rings. A recent review [1] covered all aspects related to the synthesis and properties of these materials and showed a wide spectrum of possibilities including interesting potential applications associated with the unique reactivity of this heterocycle. Among the many macromolecular structures already investigated [1] however, polyamides constitute a minor subject including essentially only (i) a detailed piece of research on furanic–aromatic homologues based on the direct polycondensation of 2,5-furandicarboxylic acid with various aromatic diamines [2] and (ii) our recent work, still in progress, on the interfacial polycondensation of a difuranic diacid chloride with various aliphatic diamines [3,4]. Still less work has been published on fully furanic polyamides, namely a couple of studies describing the interfacial polycondensation of diacid chlorides and diamines [2,4].

In another vein, a patent [5] and a short communication [6] reported within fifteen years' span the possibility of preparing a furanic polyamide based on the self-condensation of *N*-hydroxymethyl-2-furamide, viz. the acid-catalysed reaction between the OH group and the H5 atom. This approach resembles that which has been exploited for decades in order to polymerise furfuryl alcohol, but, whereas the latter polycondensation produces basically –CH_2–2,5-Fu– units (and in fact important side reactions leading to deeply coloured and cross-linked materials [7]), the former was supposed to lead to a polyamide with the simple –2,5-Fu–CO–NH–CH_2– structural unit. Unfortunately, this interesting system was not studied in detail either in terms of scientific content (mechanism, structure), or with regard to the properties of the ensuing material. The present investigation aims at filling these gaps and improving both the synthetic approach and the quality of this polyamide.

2. Experimental

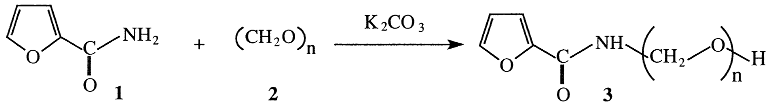
2.1. Synthesis of 2-furamide

This precursor (**1**) was prepared by the standard procedure [8] which consists in adding dropwise 20 g (0.153 mol) of 2-furoyl chloride to a solution of ammonia in diethyl ether which is kept saturated by a continuous bubbling of NH_3. The resulting white precipitate was filtered, washed first with 8 ml of ice-cold water and then with diethyl ether and finally vacuum dried at 80°C: 88% yield. FTIR (cm^{-1}, KBr pellet): 3360 (NH), 3152 (=CH, Fu), 1661 (C=O), 1561 (C=C, Fu), 1011 (furan ring breathing mode), 980 and 873 (Fu). 80 MHz ^1H NMR (δ(/TMS/DMSO-d_6): 6.57 (m, ^1H, H4, Fu), 7.07 (d, ^1H, H3, Fu), 7.36 (m, 2H, NH), 7.76 (d, ^1H, H5Fu). MP = 142°C.

---

* Corresponding author. Tel.: +33-76-826-947; fax: +33-76-826-933.
E-mail address: alessandro.gandini@efpg.grenet.fr (A. Gandini).

PII: S0032-3861(99)00538-8



Scheme 1.

2.2. Polymerisation

Two different procedures were examined in order to optimise the polymer synthesis and to gain information on the actual condensation mechanism.

2.2.1. Method A

The basic conditions were those described previously [6], but it was found that the results were not reproducible because the amount of residual moisture in the first phase (a key factor not recognised by those authors) could alter the course of the reaction. We therefore proceeded according to the following improved procedure. In the first step, 1 g (9 mmol) of **1** was mixed with 0.38 g (12.6 mmol) of paraformaldehyde, 0.027 g (0.2 mmol) of K_2CO_3 and 0.2 ml of water and heated under magnetic stirring for one hour at 75°C. This slurry turned progressively into a viscous liquid. The consumption of **1** with reaction time was followed by GLC. The mixture was then allowed to reach room temperature and the second step consisted in adding to it 2.7 ml (72 mmol) of formic acid and 3 mmol of a strong Lewis or Brønsted acid ($Et_2O{\cdot}BF_3$, H_2SO_4, p-$CH_3C_6H_4SO_3H$) and stirring the resulting polycondensation medium at 60°C for 8 h before precipitating the polyamide into an excess of water. The product was filtered and washed with water to remove all traces of acid and then suspended in refluxing ethanol for 1 h. The polymer was finally filtered, washed with diethyl ether and vacuum dried to constant weight at 80°C.

2.2.2. Method B

This procedure was elaborated as an original and more efficient alternative to method A and involved a single operation. The medium used to dissolve **1** was acidic from the start, viz. either a strong acid dissolved in formic acid, or sulphuric acid used both as solvent and catalyst. To this solution, kept at 0°C, paraformaldehyde powder was slowly added under stirring. Thereafter, the resulting homogeneous mixture was heated to 60°C and stirred for 8 h. The polyamide was isolated, purified and dried as described above for method A.

2.3. Polymer characterisation

The structure of the polyamides was assessed by FTIR and ^1H NMR spectroscopy. Their molecular weight was inferred by the inherent viscosity of their solution in *m*-cresol (C = 0.15 g/dl) at 25°C. DSC and TGA analyses were also carried out.

3. Results and discussion

3.1. Synthesis and mechanisms

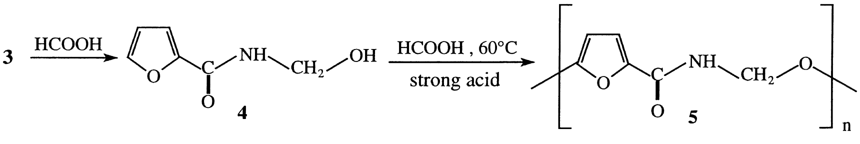
In order for method A to function properly, it is imperative to insure the correct development of the first stage which leads to the formation of **3** in a basic medium, viz.: (Scheme 1).

We found that this reaction did not take place to any appreciable extent in the absence of moisture and was difficult to reproduce in quantitative terms when the amount of residual water was not controlled. A specific series of runs was therefore conducted with different known quantities of added water in order to establish the optimum conditions relative to the yield of substitution, which are given in the experimental part above. The best results corresponded to a good selectivity and about 70% yield of **3**. It is in fact well known [9] that basic catalyses such as this one require a certain extent of hydration to activate the carbonate anions.

The second stage of the process used for method *A* involves the acid-catalysed removal of the excess of formaldehyde fixed on **1** and the subsequent acid-catalysed polycondensation of **4**: (Scheme 2).

Although the formation of intermediate **4** seems reasonable, we did not isolate it and it is equally possible that the corresponding carbenium ion is generated instead and is responsible for the subsequent polycondensation.

The second stage was followed by withdrawing samples of the reaction mixture at different times, precipitating the polymer in water and determining its inherent viscosity. Fig. 1 shows three typical results related to reactions conducted in the same conditions, but with three different strong acids. First of all, it is important to underline that formic acid catalysed the removal of the excess formaldehyde borne by **3**, but not at all the polycondensation itself



Scheme 2.

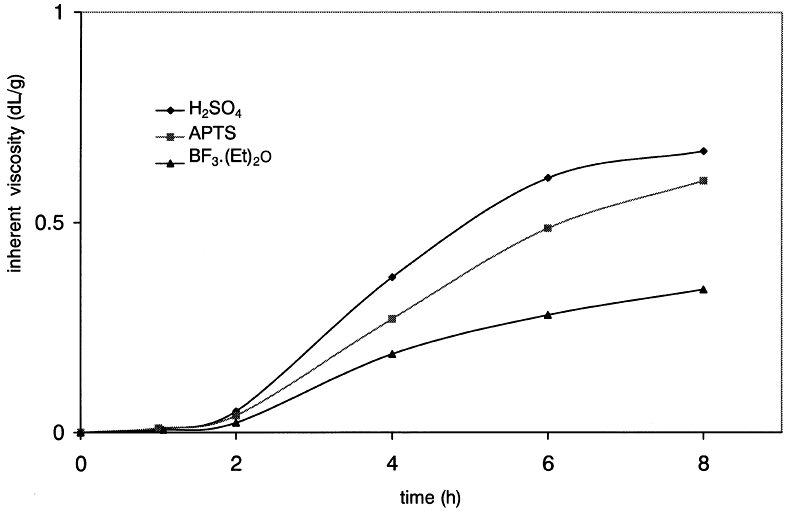


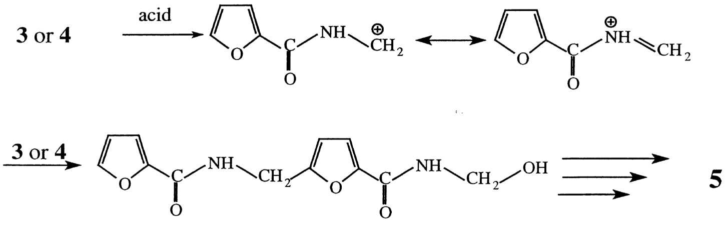
Fig. 1. Variation of the inherent viscosity of polyamide **5** as a function of the reaction time with various catalysts (method A). [**2**]/[**1**] = 1.4; [**1**]/[***cat***] = 3.0; T = 60°C. APTS = *p*-toluenesulfonic acid.

which required the intervention of a strong Lewis or Brønsted acid. The second relevant observation, related to the results summarised in Fig. 1, is the fact that all the η vs time plots are S-shaped suggesting that the loss of formaldehyde is a slow process giving rise to a progressive accumulation of the intermediate monomer. This induction period lasted about two hours in the specific conditions given in Fig. 1. A third point relates to the difference in activity of the acids used as catalysts for the polycondensation which indicates that strong Brønsted acids are more efficient than Lewis ones. The most plausible mechanism for the chain growth of the polyamide resembles that proposed for the analogous polycondensation of furfuryl alcohol [7], namely the formation of an electrophilic site on the carbon atom adjacent to the nitrogen atom, followed by its interaction with the 5 position of the heterocycle: (Scheme 3).

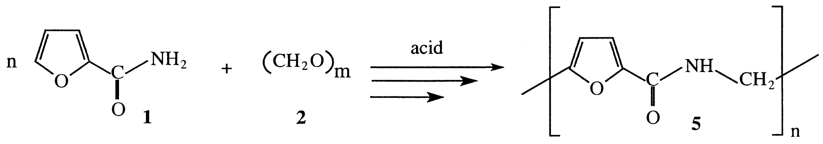
With all systems tested according to method A, the molecular weight of polyamide 5 reached a plateau value, as shown in the three examples of Fig. 1. Moreover, even with strong Brønsted acids, the inherent viscosities corresponding to this maximum DP were relatively low. We thought that unreacted **1** could be the possible cause of this drawback, since it could act as chain terminating agent by reacting with the electrophilic end of the growing chain through its 5 position. To test this hypothesis, we removed the remaining amounts of **1** from the reaction mixture, obtained at the end of the first stage by precipitating **1** into an excess of acetone, before proceeding to initiate the second stage. This test did not improve the performance of the polycondensation, which behaved as with the normal procedure. It was therefore concluded that the progressive accumulation of moisture in the reaction medium, formed in each condensation step, produced a concomitant decrease in the catalytic activity of the acid, i.e. in its aptitude to form the electrophilic centres.

The possibility of avoiding the base-catalysed addition of paraformaldehyde to **1** was then explored with the aim of simplifying the experimental conditions and trying to reach higher molecular weights. We therefore switched to method B, as described above, in order to verify whether it would be possible to induce the addition of formaldehyde (or its oligomers) to **1** by acid catalysis and thus obtain polyamide **5** in a single operation, viz.: (Scheme 4).

The preliminary tests were successful and a more systematic study was therefore conducted. Table 1 gives the experimental data related to the series of runs which were carried out according to method B together with the inherent viscosities obtained for each ensuing polymer. Figs. 2–4 complete the illustration of the features of this method as a function of the variables studied to date.



Scheme 3.



Scheme 4.

The results obtained from this series of experiments lead to the following conclusions:

1. Method B is undoubtedly much more interesting than method A in terms of maximum molecular weights, whereas the kinetic features are very similar in both instances. Fig. 2 shows in fact that with sulphuric acid as catalyst, η is nearly three times higher with method B although all the conditions are the same. This observation suggests that in the first stage of method A some unwanted reaction(s) took place (e.g. the involvement of the C5 position of **1**) which caused negative repercussions in the second (polymerisation) stage.
2. All the runs gave S-shaped curves with induction periods of about 2 h, as in the case of method A (see Fig. 1), which suggests that the new technique did not alter the kinetic features of the system.
3. The different Lewis and Brønsted acids used as catalysts gave similar kinetics, but very different molecular weights, closely related to the strength of the acid, as expected for a system which accumulates water as the reaction progresses. Thus, the lower the strength of the acid, the more difficult will be its likelihood to sustain the electrophilic centres, as the water concentration increases.

Table 1
Experimental conditions and final inherent viscosity of the ensuing polyamide **5**, related to polymerisations carried out according to method B

Solvent	Catalyst	[**2**]/[**1**]	Temperature (°C)	η (dl/g)
HCOOH	H_2SO_4	1.2	60	1.62
	APTS			1.45
	$(Et)_2O\cdot BF_3$			1.15
	$SnCl_4$			0.50
	CF_3COOH			0.20
HCOOH	$(Et)_2O\cdot BF_3$	0.75	60	0.10
		1		0.70
		1.25		1.02
		1.5		1.16
		2		1.25
H_2SO_4	H_2SO_4	0.75	60	0.15
		1		1.38
		1.25		1.98
		1.5		2.34
		2		2.36
HCOOH	$(Et)_2O\cdot BF_3$	1.5	20	0.55
			40	0.70
			60	1.16
			80	1.80
H_2SO_4	H_2SO_4	1.5	20	1.04
			40	1.70
			60	2.34
			80	[a]
HCOOH	H_2SO_4	1.5	20	0.80
			40	1.05
			60	1.50
			80	2.10

[a] Insoluble product.

4. The molar ratio between the reagents is a determining factor in the way the polycondensation takes place, as shown in Fig. 3. The best results were obtained with [**2**]/[**1**] = 1.5–2, both with formic and sulphuric acid as solvent. For ratios higher than 2.5, the reaction medium gelled within a couple of hours, suggesting that serious side reactions associated with the insertion of formaldehyde at unwanted sites of the monomer and/or the polymer began to take place and gave rise to branching and finally cross-linking.
5. The medium used for these polycondensations is another important aspect for two reasons: first because of the essential role of the solvent in terms of solvating the electrophilic intermediates (thus nucleophilic solvents are to be avoided) and secondly because of its capacity to keep the polyamide in solution even for high molecular weights. The obvious choice was therefore to use Brønsted acids as solvents. Both mild and strong homologues were tested and Table 1 reports the most relevant experiments in which either formic or sulphuric acid were used. As already pointed out, Fig. 2 shows that in formic acid, the different catalysts displayed a positive (albeit variable) activity and in all instances **5** remained in solution until the end of the polymerisation. Fig. 3 shows the behaviour of a series of experiments in which sulphuric acid was employed both as the solvent and as the catalyst and the results obtained clearly indicate that this medium was more effective in terms of the molecular weight of the resulting polyamide. However, whereas the polymers obtained in formic acid bore a creamy colour, those isolated from sulphuric acid were deep brown. The origin of the latter coloration is unclear, but it does not seem to be associated with serious side reactions, since the polymers remain soluble and have indeed quite high molecular weights. This point is presently being examined.
6. The final parameter studied was the reaction temperature. Fig. 4 shows that in the three series of experiments, carried out to test this factor, an increase in temperature produced a corresponding increase in the molecular weight of **5**. In formic acid as solvent, this effect became more pronounced at the higher temperatures, whereas in sulphuric acid, as the temperature was raised above 60°C,

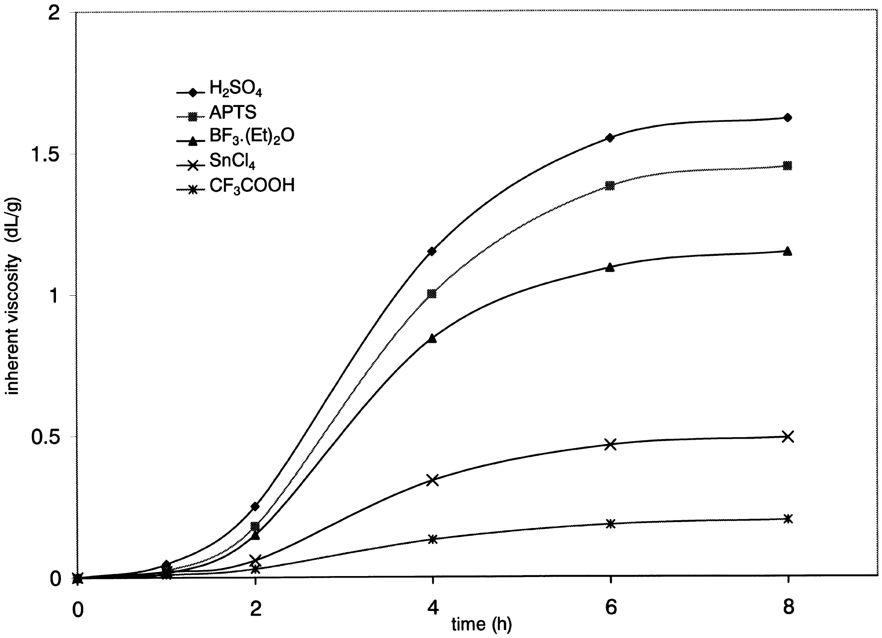


Fig. 2. Variation of the inherent viscosity of polyamide **5** as a function of the reaction time with various catalysts (method B). [**2**]/[**1**] = 1.2; [**1**]/[***cat***] = 3.0; $T = 60$°C. APTS = *p*-toluenesulfonic acid.

the polymer turned progressively less soluble and more deeply coloured, i.e. side reactions started playing a detrimental role.

3.2. Characterisation of polyamide 5

The ^{1}H NMR spectrum of polyamide **5** gave the following resonances (δ, ppm/DMSOd$_6$/TMS): 4.43 (2H, C*H*$_2$), 7.12 (^{1}H, *H*3-Fu),6.37 (^{1}H, *H*4-Fu), 8.77 (CON*H*). The FTIR of polyamide 5 was also entirely consistent with the structure of this furanic polyamide (cm^{-1}, KBr): 3370 and 3200 (hydrogen-bound NH), 2920 (CH$_2$), 1660 (amide I C=O), 1540 and 1330 (amide II and III: δN–H and νC–N coupling), 1580 (C=C, Fu), 1020 (furan ring breathing), 975, 810 and 760 (2,5-disubstituted furan rings). Both spectra were typical of all samples prepared, irrespective of their DP.

The TGA tracings of various samples of **5**, obtained in a

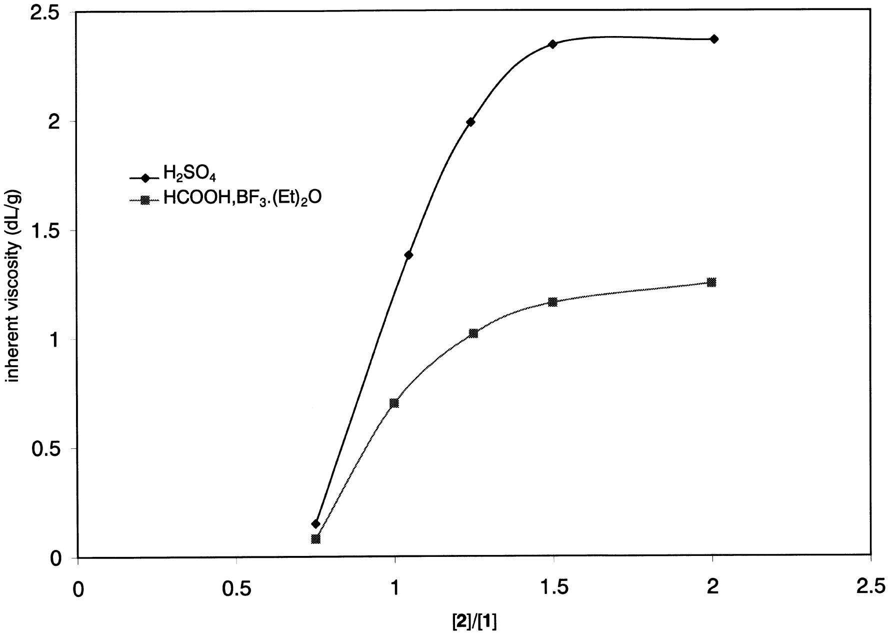


Fig. 3. Variation of the inherent viscosity of polyamide **5** as a function of the paraformaldehyde-to-2-furamide molar ratio with two different catalysts in different media (method B). [**1**]/[***cat***] = 3.0; $T = 60$°C; reaction time: 8 h.

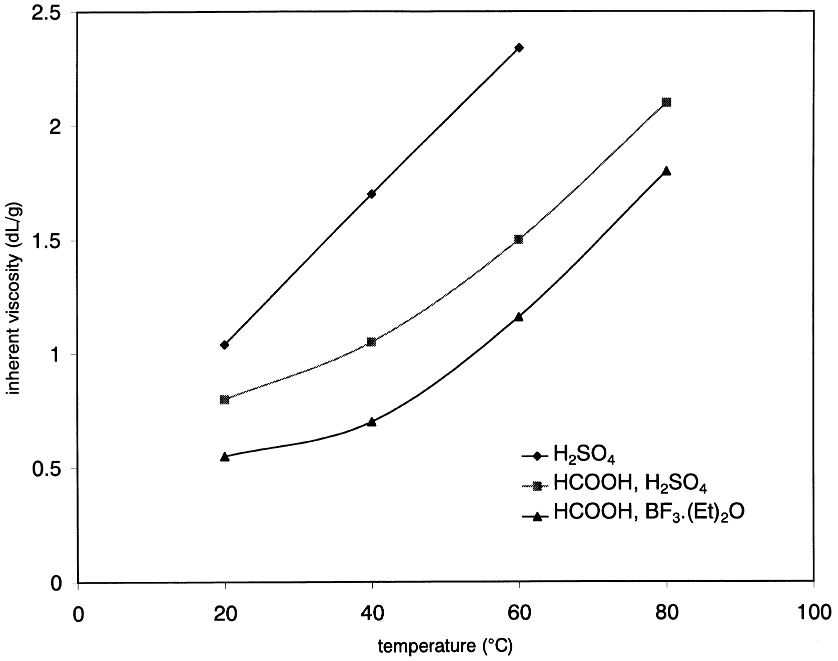


Fig. 4. Variation of the inherent viscosity of polyamide **5** as a function of the reaction temperature with different catalysts and media (method B). [**2**]/[**1**] = 1.5; [**1**]/[***cat***] = 3.0; reaction time: 8 h.

nitrogen atmosphere with a heating rate of 20°C/min, showed that this novel polyamide is stable up to 250°C and then degrades between 300 and 500°C leaving 30 to 35% of carbonaceous residue.

The DSC analysis of **5** was carried out under nitrogen with heating and cooling rates of 10°C/min. All materials were amorphous and displayed a glass transition between 65 and 75°C, depending on the sample.

4. Conclusion

The use of a relatively simple original synthetic procedure, based on the exclusive intervention of an acidic catalyst, has provided a means of preparing a 2,5-furanmethylene polyamide of regular structure and high molecular weight. Work is in progress to attempt further improvement of the DP and of the quality of this material and to characterise its physical properties.

References

[1] Gandini A, Belgacem MN. Progr Polym Sci 1997;22:1203.
[2] Mitiakoudis A, Gandini A. Macromolecules 1991;24:830.
[3] Gharbi S, Gandini A. Acta Polym 1999;50:293.
[4] Abid M, Gharbi S, El Ghrbi R, Gandini A. Submitted for publication.
[5] Moldenhauer O, Irion W, Marwitz HO. German Patent, 1013425, 1953.
[6] Mihajlov VM, Peeva N. Makromol Chem 1968;116:107.
[7] Choura M, Belgacem MN, Gandini A. Macromolecules 1996;29:3839.
[8] Vargha M, Gönezy S. J Am Chem Soc 1950;72:2738.
[9] Le Bigot Y, Delmas M, Gaset A. Tetrahedron 1986;42:1.