Polymer Vol. 39 No. 20, pp. 4751–4755, 1998

0032-3861/98/$19.00+0.00

PII: S0032-3861(97)10120-3

Some aspects of preparation of fluorine-containing polyimides

P. Sysel[a,*], **M. Sochůrek**[a] **and P. Holler**[b]
[a]*Department of Polymers, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic*
[b]*Institute of Macromolecular Chemistry, Heyrovsky sq. 2, 162 06 Prague 6, Czech Republic*
(Received 15 July 1997; revised 24 September 1997; accepted 24 September 1997)

Polyimides based on 4,4′-(hexafluoroisopropylidene)diphthalic anhydride and 4,4′-(hexafluoroisopropylidene)-dianiline with controlled and uncontrolled molecular weight were prepared. The products with controlled molecular weight were terminated with 4-*tert*-butylaniline. The synthesized poly(amic acid)s were transformed into polyimides using both thermal solid state and solution imidization. Molecular parameters of the prepared polymers were evaluated by viscometry, size exclusion chromatography and n.m.r. spectroscopy. The properties of polyimides prepared by both methods were compared. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: fluorine-containing polyimides; poly(amic acid)s; molecular weight)

INTRODUCTION

Aromatic polyimides (PI) (*Figure 1*) exhibit very good dielectric, chemical and mechanical resistance at elevated temperatures[1]. When fluorine atoms (or groups containing these atoms) are incorporated into the polyimide structure, some additional properties are also improved, e.g. water sorption, the dielectric constant and optical losses (in optoelectronic components) are all reduced[2]. On the other hand, reactivity of the fluorine-containing diamines towards dianhydrides (*Figure 1*) (nucleophilic substitution on the carbon atom of the carbonyl group with the amine[3]) diminishes due to the electron-withdrawing effect of the electronegative fluorine atoms. In some cases it can then be difficult to prepare polyimide films with the desired properties from such materials[2].

Properties of polymers are generally governed by their structure (chemical composition, morphology, etc.) and by their molecular weight. From this point of view it is very important to be able to evaluate correctly the molecular weight of the prepared fluorine-containing polyimide precursors (poly(amic acid)s, PAA (*Figure 1*)) and polyimides (of known chemical compositions). Size exclusion chromatography (SEC) has been mainly used so far[2,4]. However, calibration that relies on polystyrene standards provides relative values of molecular weight only.

In this work we synthesized 4-*tert*-butylaniline-terminated poly(amic acid)s and polyimides, based on the most often used fluorine-containing monomers 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 4,4′-(hexafluoroisopropylidene)dianiline (6FDAM)[2,4] with controlled molecular weight (*Figure 2*). Their number-average molecular weights M_n were determined by ^{1}H n.m.r. spectroscopy and intrinsic viscosities $[\eta]$ by viscometry. The relationship between M_n and $[\eta]$ was used to determine the molecular weights of PAA and PI based on 6FDA and 6FDAM with uncontrolled molecular weight up to $M_n = 25\,000\ \mathrm{g\ mol^{-1}}$. Some correlations between these parameters and reaction conditions of their preparation were found. Some selected properties of the prepared polyimides were also evaluated.

EXPERIMENTAL

Materials

4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) (Aldrich) was heated overnight to 160°C in a vacuum before use. 4,4′-(Hexafluoroisopropylidene)dianiline (6FDAM) and 4-*tert*-butylaniline (*t*-BA) (both Aldrich) were used as received. 1,4-Bis(4-amino-1,1-dimethylbenzyl)benzene (Bisaniline P, BIS P) (Mitsui Petrochemical Industries, Ltd.) was used as received.

N-Methyl-2-pyrrolidone (NMP) and 1,2-dichlorobenzene (DCB (both Merck) were distilled under vacuum over phosphorus pentoxide and stored in an inert atmosphere. Chloroform (Lachema, Czech Republic) was distilled over phosphorus pentoxide.

Synthesis of poly(amic acid)s

A typical example of the synthesis of the 4-*tert*-butylaniline-terminated poly(amic acid) (with theoretical molecular weight $M_n = 10\,000\ \mathrm{g\ mol^{-1}}$) is as follows: 6FDA (5 g, 0.01126 mol) was dissolved in 58.6 ml NMP in a 250 ml four-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser with drying tube. *t*-BA (0.2606 g, 0.00175 mol) (+ 10 ml NMP) was added and allowed to react with the 6FDA for 4 h. 6FDAM (3.4704 g, 0.01038 mol) (+ 10 ml NMP) was added to the reaction mixture. The reaction was allowed to proceed for 48 h at room temperature.

During preparation of PAA with uncontrolled molecular weight a diamine was put into the flask first and no terminating agent was used.

---

[*] To whom correspondence should be addressed

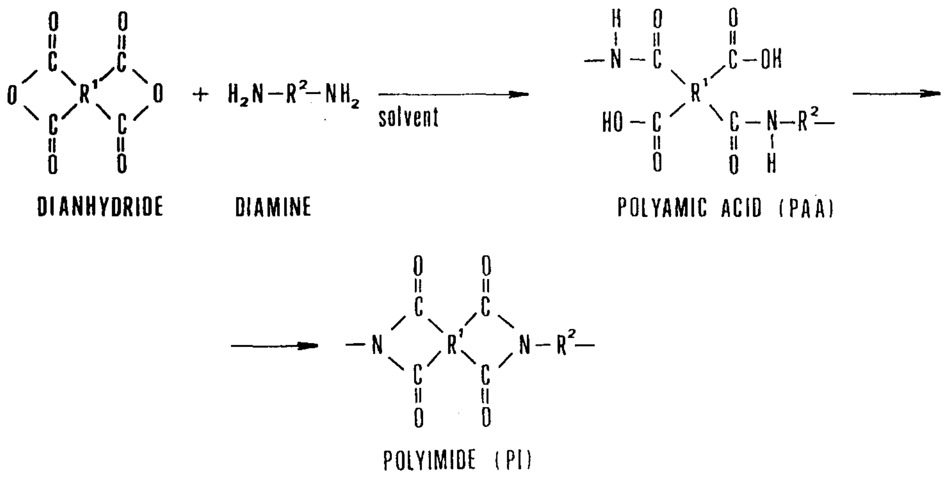

Figure 1 Synthesis of polyimides

Preparation of polyimides

Solid-state thermal imidization. The solution of poly(amic acid) was diluted with NMP and precipitated into distilled water. The collected PAA was dried in a vacuum desiccator for 72 h at room temperature.

Solid PAA was placed into a small ground joint flask fitted with a vacuum inlet and heated under vacuum in a heating block at 80°C for 1 h, 120°C for 1 and 250°C for 2 h, and subsequently 1 h at a final temperature (variants 260, 300 and 350°C).

Thermal solution imidization. A 250 ml four-necked flask containing a 10 wt% solution of poly(amic acid) in NMP was equipped with a mechanical stirrer, a nitrogen inlet, an azeotrope trap (filled with DCB), a condenser with drying tube and a thermometer. After adding 12.0 ml DCB the reaction mixture was heated to 180°C (in an oil bath) for 48 h. The solution was cooled to room temperature, diluted with NMP and precipitated into a mixture of methanol and distilled water. The collected polyimide was dried to constant weight in a vacuum oven (at 160°C for 24 h).

Film preparation

A 10 wt% polyimide solution in chloroform was cast onto a glass plate and the solvent evaporated slowly at room

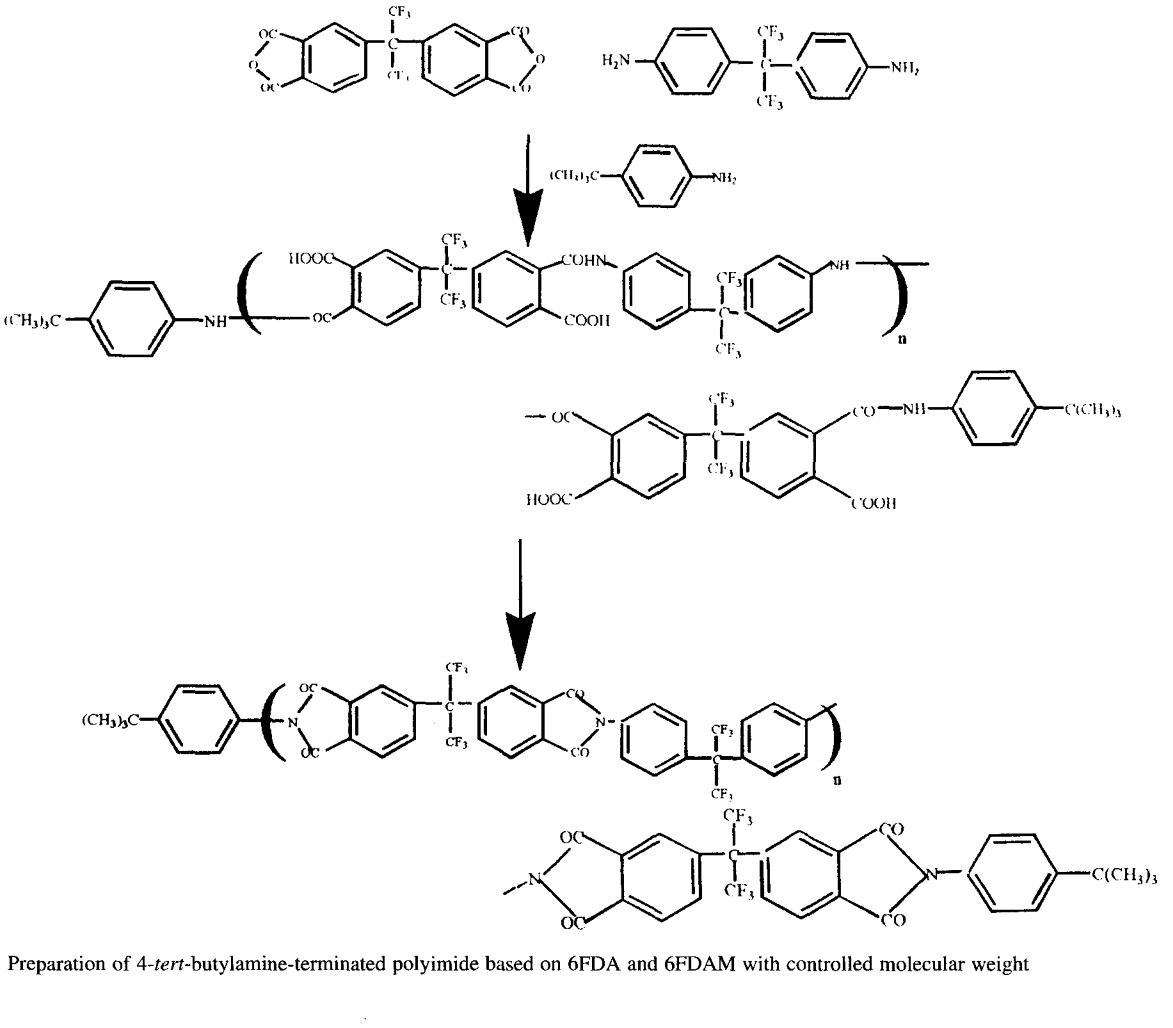

Figure 2 Preparation of 4-*tert*-butylamine-terminated polyimide based on 6FDA and 6FDAM with controlled molecular weight

Table 1 Experimental conditions of SEC analyses

	PAA	PI
Column	Labio GM 1000 500 × 8 mm	PL-gel mixed 5 μm 300 × 8 mm
Mobile phase	NMP + 0.5 wt% LiCl at 1 ml min^{-1}	Chloroform at 0.5 ml min^{-1}
Detector	U.v. (254 nm) HP 1030B	ELSCD[a] PLEMD-90
Standards	Polystyrenes	Polystyrenes

[a] Evaporative light scattering concentration detector

temperature. The film was removed from the plate and heated for 2 h at 200°C in a vacuum oven. The final thickness of homogeneous films was 30 μm.

Methods

The terminated poly(amic acid)s (in *d*-dimethylsulfoxide) and polyimides (in *d*-chloroform) were characterized by ^{1}H n.m.r. (BRUKER 400 spectrometer operating at 400.134 MHz, 256 scans).

Intrinsic viscosities of all polymers were measured in NMP (PAA) or chloroform (PI) at 25°C. Molecular weights of the selected PAA and PI were determined by using size exclusion chromatography (SEC). Experimental conditions of SEC analyses are given in *Table 1*.

RESULTS AND DISCUSSION

Poly(amic acid)s and polyimides with controlled molecular weight

Evaluation of molecular weights of PAA and PI based on 6FDA and 6FDAM with uncontrolled molecular weight was one of the important objectives of this work.

Table 2 Molecular parameters of PAA and PI with controlled molecular weight

PAA/PI	$M_{\mathrm{n,theor}}^{a,b}$ (g mol^{-1})	$M_{\mathrm{n,n.m.r.}}$ (g mol^{-1})	$[\eta]^c$ (ml g^{-1})
PAA	7500	7800	4.9
PAA	10000	12400	8.4
PAA	15000	14600	12.3
PAA	20000	21000	16.8
PAA	25000	27000	20.8
PI	7500	5300	1.1
PI	10000	10600	2.6
PI	15000	16400	5.7
PI	20000	17600	7.2
PI	25000	23800	10.4

[a] Calculated from the molar ratio of monomers
[b] Water loss during PAA → PI transformation was ignored
[c] For PAA in NMP at 25°C, for PI in chloroform at 25°C

Molecular weights of polymers are almost exclusively evaluated from solution properties. Viscometry is the easiest method for this purpose. Unfortunately, the parameters *K* and *a* of the Mark–Houwink equation $[\eta] = KM_{\mathrm{v}}^{a}$ (where M_{v} is a viscosity-average molecular weight) for these types of PAA and PI have not been found. Moreover, polyimide standards for the SEC analysis are not available and calibration based on polystyrene standards provides relative values only[2,4].

We therefore synthesized the 4-*tert*-butylaniline-terminated PAA and PI based on 6FDA and 6FDAM (*Figure 2*) with controlled number-average molecular weights M_{n} in the range 7500–25 000 g mol^{-1}. The values of M_{n} were obtained from the integral ratio of the methyl groups of the terminating agent (~1.3 ppm) to the aromatic protons of polyimide moieties (at 7–8.5 ppm) (*Figure 3*). This method provides less reliable results of M_{n} for polymers

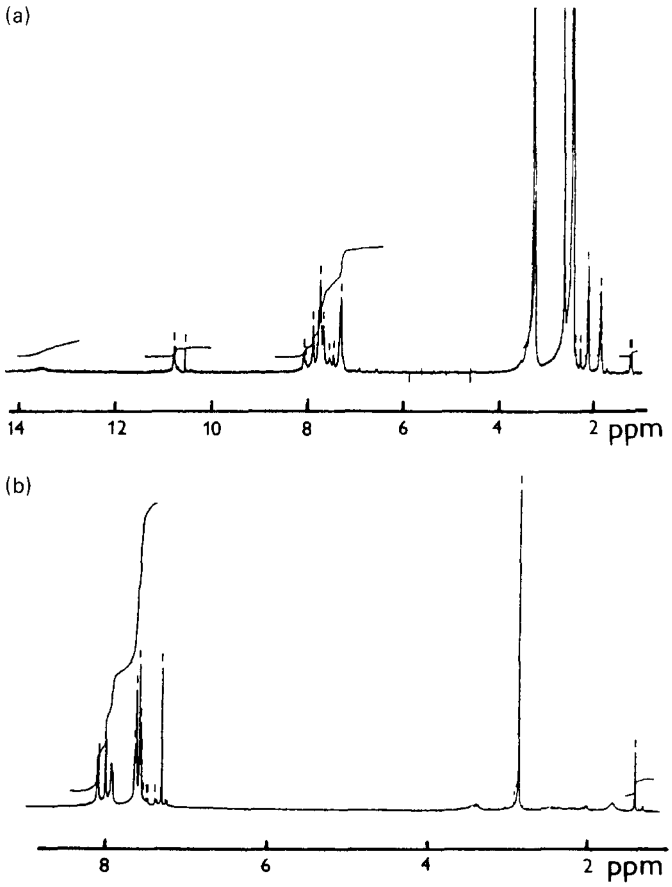

Figure 3 ^{1}H n.m.r. spectra of 4-*tert*-butylaniline-terminated PAA (a) and PI (b) based on 6FDA and 6FDAM with controlled molecular weight

Table 3 Dependence of intrinsic viscosity on reaction time for PAA with uncontrolled molecular weight

Reaction time (h)	$[\eta]$ (ml g^{-1})
1	6.6
2	6.4
5	5.9
8	12.5
12	17.3
15	17.7
18	16.4
24	18.4
32	19.1
42	20.5
50	20.6

with a higher molecular weight owing to the unfavourable signal-to-noise ratios at 1.3 ppm. Intrinsic viscosity was also determined for each polymer and the relationship $M_n - [\eta]$ was obtained in this way. All data are summarized in *Table 2*.

Synthesis and characterization of poly(amic acid)s and polyimides with uncontrolled molecular weight

An equimolar ratio of dianhydride and diamine and no endcapping agent was used for the preparation of PAA and PI based on 6FDA and 6FDAM with uncontrolled molecular weight.

Table 3 shows the dependence of the intrinsic viscosity on the reaction time for this kind of PAA. Intrinsic viscosity rises with reaction time up to 50 h, more rapidly in the interval 5–12 h than in the region 12–50 h.

The final value of $[\eta] = 20.6$ ml g^{-1} corresponds approximately to $M_n = 25\,000$ g mol^{-1} (see *Table 2*). This is markedly lower than the value $[\eta] = 60$ ml g^{-1} obtained for PAA based on 6FDA and 1,4-bis(4-amino-1,1-dimethylbenzyl)benzene (BIS P) (*Figure 4*), synthesized under the same reaction conditions. Unfortunately, we were unable to set up a 'calibration' relationship $[\eta] - M_n$ for such high values of $[\eta]$. Nevertheless, it is possible to estimate from the similarity of this relationship up to $M_n = 25\,000$ g mol^{-1} for PAA based on 6FDA/BIS P and 6FDA/6FDAM that the rigidity of their polymer chains is also not markedly different. Consequently, the higher $[\eta]$ of 6FDA/BIS P PAA should be given mainly by its higher M_n in comparison with 6FDA/6FDAM PAA.

In summary, circumstantial evidence about lower reactivity of fluorine-containing diamine in comparison with diamine which does not contain fluorine atoms has been obtained.

Some of the 6FDA/6FDAM PAA samples were also evaluated by SEC analysis (*Table 4*). The $M_{n,SEC}$ are 1.5–1.75 times higher than $M_{n,n.m.r.}$. The reason can be different solubility of PAA and polystyrene standards in NMP and/or a repulsive interaction of PAA with the column packing. Although lithium chloride was added into the mobile phase, a polyelectrolyte effect can still occur. On the other hand, the ratio $M_{n,SEC(PAA1)}/M_{n,SEC(PAA2)}$ is quite close to $M_{n,n.m.r.(PAA1)}/M_{n,n.m.r.(PAA2)}$ or $[\eta]_{PAA1}/[\eta]_{PAA2}$. The ratio M_w/M_n (where M_w is a weight-average molecular weight) was slightly lower than 2.

Table 5 Molecular parameters of polyimides prepare by thermal solid state imidization from PAA with $[\eta] = 18.4$ ml g^{-1}

T^a (°C)	$[\eta]^b$ (ml g^{-1})	$M_{n,SEC}{}^c$ (g mol^{-1})	M_w/M_n
260	14.8	9300	2.9
300	16.6	8300	3.0
350	25.5	19600	3.4

^{a}Final imidization temperature (1 h)
^{b}In chloroform at 25°C
^{c}Mobile phase chloroform, polystyrene standards

Table 4 Comparison of molecular weight M_n of PAA obtained by different methods

Sample	$M_{n,n.m.r.}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	M_w/M_n	$[\eta]$ (ml g^{-1})
PAA 1	7800	11200	1.9	4.9
PAA 2	12400	21800	1.7	8.4

The increasing final (imidization) temperature influences favourably the molecular parameters of polyimides prepared by the thermal solid state imidization (*Table 5*). The intrinsic viscosity $[\eta] = 25.5$ ml g^{-1} obtained at 350°C is more than two times higher than the value $[\eta] = 10.4$ ml g^{-1} corresponding to $M_n = 25\,000$ g mol^{-1} (see *Table 2*). It is obvious from the i.r. spectra that the transformation of PAA into PI is almost complete at all three final imidization temperatures. This is very important because the conclusion about the change of molecular weight from the change of intrinsic viscosity is applicable only to identical polymer structures analysed under constant experimental conditions. When PAA based on 6FDA and BIS P with $[\eta] = 60$ ml g^{-1} was imidized under the same reaction conditions, a polyimide with $[\eta] = 48$ ml g^{-1} was obtained.

The absorbance band of the anhydride groups at 1850 cm^{-1} becomes less intensive with increasing temperature in the i.r. spectra. The increase in the intrinsic viscosity combined with a simultaneous decrease in the content of anhydride groups leads us to a conclusion about a favourable effect of the chain extension at sufficiently high imidization temperatures.

The thermal solution imidization was successfully used for transformation of some PAA into PI[5]. This 'one pot' synthesis was realized under homogeneous conditions at relatively low temperatures (~200°C).

Although the polyimide based on 6FDA and 6FDAM is only marginally soluble in NMP, it forms a transparent solution in the solvent mixture NMP/DCB even when cooled to room temperature. The dependence of the molecular parameters (including solubility) on the imidization time for the products prepared by solution imidization at 180°C is shown in *Table 6*. It is apparent that it is not possible to prepare a sufficiently high-molecular-weight PI based on 6FDA and 6FDAM by this procedure under the experimental conditions employed ($[\eta] = 41$ ml g^{-1} for the PI based on 6FDA and BIS P).

Imidization of PAA proceeds via a nucleophilic attack on

Table 6 Molecular parameters of products prepared by thermal solution imidization from PAA with $[\eta] = 18.4$ ml g^{-1}

t^a (h)	$[\eta]$ (ml g^{-1})		$M^b_{n,SEC}$ (g mol^{-1})		M_w/M_n	Solubility^c	
	Solvent		Mobile phase			Solvent	
	NMP	$CHCl_3$	NMP	$CHCl_3$		NMP	$CHCl_3$
0 (PAA)	18.4	–	–	–	–	S	IS
1	6.5	–	–	–	–	S	IS
3	6.0	–	11900	–	–	S	IS
8	8.5	–	–	–	–	S	MS
12	10.5	–	–	–	–	MS	MS
18	15.7	4.6	–	2100	2.4	MS	S
24	14.7	5.1	–	2400	2.3	MS	S
28	9.3	5.6	–	2400	2.3	MS	S
48	–	7.7	–	2500	2.5	MS	S

^{a}Imidization time
^{b}Polystyrene standards
^{c}S = soluble, I = insoluble, MS = marginally soluble

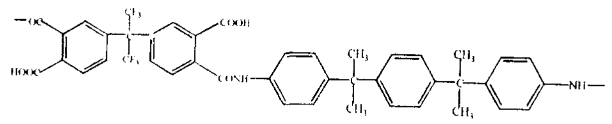

Figure 4 Poly(amic acid) based on 6FDA and BIS P

the carbon atom of the carbonyl group by the free electron pair of the amide nitrogen[3] (*Figure 1*). The imidization rate is thus influenced by the spreading of the electron density along the chain of PAA, which in turn depends on the nature of the monomers utilized and the reaction intermediates. It is apparent from our results that the fluorine-containing diamine influences the synthesis of both PAA and PI. In addition, the moderate experimental conditions of solution imidization do not allow PI films with desirable properties to be prepared.

A drop in intrinsic viscosity was observed at the beginning of solution imidization (see *Table 6*). In the range between 1 and 18 h this phenomenon cannot be connected with deteriorating thermodynamic quality of the solvent for products with a higher degree of imidization because the decrease (1–3 h) is followed by an increase (3–18 h). It seems that PAA undergoes chain cleavage especially during the initial stages of the process. A shift in the equilibrium monomers/PAA and/or hydrolysis of amide bonds in the polymer backbone may be responsible for this splitting[5]. On the other hand, the drop in intrinsic viscosity of the products obtained after 18 h and longer can probably be explained by poor thermodynamic quality of the solvent (NMP) towards fully imidized polymers.

The molecular weights of polyimides prepared by both thermal solid state and solution imidization as determined by SEC (*Tables 5 and 6*) are lower in comparison with our estimate based on the $[\eta] - M_n$ 'calibration'. The reasons underlying this discrepancy can be similar as in case of the SEC analysis of PAA with the exception of the polyelectrolyte effect. The ratio M_w/M_n ranged from 2.3 to 3.4.

Table 7 Comparison of properties of polyimides prepared by different imidization methods

Property	Imidization Solid state	Solution
$[\eta]$ (ml g^{-1})[a]	25.5	7.7
Density (g cm^{-3})[b]	1.37	1.21
Water sorption (wt%)[c]	1.6	3.2
Refractive index[d]	1.693	1.684
T_g (°C)[e]	330	250
T_5 (°C)[f]	463	375
Film[g]	yes	no

[a] In chloroform at 25°C
[b] By a pycnometer
[c] At 100% RH
[d] By an Abbe refractometer
[e] Glass transition temperature
[f] Temperature of 5 wt% loss
[g] Self-standing form

Some selected properties of polyimide films prepared by both thermal solid state and solution imidization are listed in *Table 7*. Differences in the ability to form self-standing films, the glass transition temperature, the temperature corresponding to a 5 wt% weight loss and water sorption all support our opinion about the lower molecular weight (and therefore a larger free volume) of the product of solution imidization.

ACKNOWLEDGEMENTS

This work was supported by grant 112157102 of the Institute of Chemical Technology, Prague.

REFERENCES

1. Sroog, C. A., *Progr. Polym. Sci.*, 1991, **16**, 561.
2. Hougham, G., Tesoro, G. and Shaw, J., *Macromolecules*, 1994, **27**, 3642.
3. Pyun, E., Mathisen, R. J. and Sung, C. S. P., *Macromolecules*, 1989, **22**, 1174.
4. Husk, G. R., Cassidy, P. E. and Gebert, K. L., *Macromolecules*, 1988, **21**, 1234.
5. Kim, Y. J., Glass, T. E., Lyle, G. D. and McGrath, J. E., *Macromolecules*, 1993, **26**, 1344.