

ORIGINAL ARTICLE

Danuta Sęk · Ewa Schab-Balcerzak · Eugenia Grabiec
Henryk Janeczek · Marc J. M. Abadie

Photochemical modification of some polynaphthalimides

Received: 25 August 2000 / Reviewed and accepted: 28 August 2000

Abstract A series of polynaphthalimides from dinaphthalene dianhydride and aromatic diamines mainly with alkyl substituents at ortho position to amine groups along with the model compounds has been synthesized using one-step high temperature polycondensation. It was found that in the case of the model compounds and the polymers synthesized from diamines with alkyl groups having at α carbon two hydrogen atoms, cyclodehydration process can take place during heating or UV irradiation and formation of additional cycle of pyrrole structure was observed. The polynaphthalimides synthesized from aromatic diamines substituted with alkyl groups can be modified under heating or UV irradiation, towards additional ring formation of pyrrole type, which causes an increase of the polymers glass transition temperatures.

Keywords Polynaphthalimides · Naphthoylenebenzopyrroles

Introduction

Polyimides, due to their high thermal stability, good mechanical properties and dielectrical resistance play an important role in the group of thermostable polymers. Because of six-membered rings in most cases exhibit higher thermal stability than five membered rings, we have started investigations on polynaphthalimides [1–4].

We found that six membered anhydride of 1,8-naphthalene type reacted with aromatic amine group neither in protic nor in aprotic solvents below 140°C, so the one step high temperature polycondensation had to be used.

The polynaphthalimides synthesized from unsubstituted aromatic diamines were soluble in some organic solvents but it was not possible to detect their glass transition temperatures using DSC method. In order to lower the Tg and improve solubility in organic solvents, alkyl substituted aromatic diamines were applied to polynaphthalimides synthesis.

Results and discussion

Introduction of the alkyl substituted diamines significantly lowers the glass transition temperatures of the polynaphthalimides in comparison to their unsubstituted analogues for which it could not be possible to detect Tg up to the decomposition onset (above 430°C) [3]. The results are presented in Table 1.

It seems to be interesting that the introduction of relatively small methyl groups causes such an effect. We suppose that in the case of unsubstituted amines there is a possibility to form some kind of H-bond which can influence the rigidity of the polymer chain. The calculated data (2) of the distance between oxygen atom in the lactone ring and the hydrogen atom in the phenyl ring (being less than 2.5 Å) does not exclude it. The introduction of the substituents disables similar interaction.

However it was found that the prolongation of the polycondensation reaction over 18 h used for polymer synthesis, caused the Tg increase of the polymer from 2,3,5,6-tetramethyl-1,4-phenylene diamine. Such behaviour was not observed in the polymer with isopropyl groups. To explain this, the model compound synthesized from 2,6-dimethylaniline and 4-benzoyl-1,8-naphthalene anhydride was investigated. The results confirmed that during longer heating of the naphthalimid, cyclodehydration reaction can take place and additional ring of pyrrole structure is formed (Fig. 1).

The same reaction observed in the model compounds are likely to proceed in a polymer chain and formation of semiladder structure should cause an increase of the polymer glass transition temperature.

D. Sęk (✉) · E. Schab-Balcerzak · E. Grabiec · H. Janeczek
Centre of Polymer Chemistry, Polish Academy of Sciences,
34 M. Curie-Skłodowska St., 40-819 Zabrze, Poland
e-mail: polymer@uranos.cto.us.edu.pl

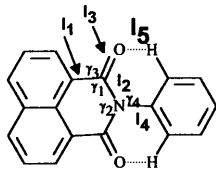
M.J.M. Abadie
LEMP/MAO, University of Montpellier,
34095 Montpellier, CEDEX 5, France

Table 1 Structures and glass transition temperatures of polynaphthalimides (Polycondensation reaction conditions. Solvent: m-cresol conc. 0.1 mol/l. Catalyst: benzoic acid and isoquinoline added after 8 hr of reaction. Total time of reaction: 18 h)

Structure of polymer	T _g [°C]
	113.9
	ND*
	ND*
	192.6
ND* not detected using DSC	

Table 2 Bond length values in imide structure

Calculated data	Structure
bond length [$\times 10^{-10}$ m] l ₁	1,514
— — l ₂	1,361
— — l ₃	1,222
— — l ₄	1,426
distance [$\times 10^{-10}$ m] l ₅	2,478



Thermal modification of alkyl-substituted polynaphthalimides

In order to prove it a series of the polynaphthalimides from various alkyl substituted diamines was synthesized. The polycondensation was carried out at 180°C in HMPT using diamines hydrochlorides to avoid cis imide formation [4]. The changes of the polymers glass transition temperatures in dependence on reaction time are presented in Table 3.

It can be seen that the prolongation of the reaction time caused the increase of the glass transition temperatures of the polymers while their reduced viscosities changed very little and their solubility did not change after heating. These results seem to confirm a stiffening of the polymer chains due to semiladder structure formation. The biggest increase of the glass transition temperature – about 150°C after heating during 100 h was observed for the polymer from 2,3,5,6-tetramethyl-1,4-phenylenediamine. The polymers synthesized from diamines with methylene group between the phenylene rings exhibited a bit smaller increase of T_g – about 70°C.

Photochemical modification of alkyl-substituted polynaphthalimides

Cyclodehydration of alkynaphthalimides was also observed to occur under UV irradiation similar to process described by Kanaoka [5, 6] for five member imide ring. In our study the model compounds and polymers having methyl and ethyl substituents were investigated at different temperatures using differential photocalorimetry (DPC). The results of DPC measurements are shown in Table 4.

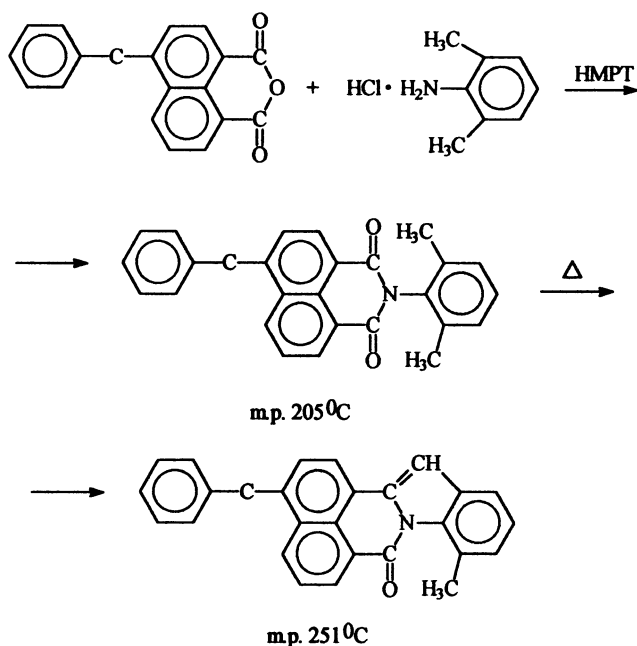


Fig. 1 Scheme of the reaction

Table 3 Glass transition temperature of the polymers versus reaction time

Polymer structure	η_{red} [dl/g]	T _g [°C]* after reaction time		
		24 h	48 h	100 h
	0.80	114	114	-
	0.58	245	296	404
	0.86	259	289	-
	0.66	265	279	337
	0.80	258	266	328
* Detected by DSC (II run)				

Table 4 Temperatures of the maximum value of the rate constant

Structure	R = -CH ₃		R = -C ₂ H ₅	
	k _{max} [1/min]	Temp. of k _{max} [°C]	k _{max} [1/min]	Temp. of k _{max} [°C]
	4.9	55	7.2	40
	1.3	50	1.7	40
	0.9	70	1.4	65
	1.2	75	-	-
*measurements performed in differential photocalorimeter DuPont 2100, mercury lamp 5.0 mW/cm ² , sample conc. 0.5 mmol/cm ³ in HMPT				

The temperatures of the maximum rate constant k for the model compounds having ethyl groups are lower than for the ones with methyl groups. It is necessary to add that the values obtained from photocalorimetry measurements concern the total process without determination of

the particular reaction steps (biradical formation, cyclization and dehydration). Nevertheless, they give an idea of the ability of the alkyl groups to the cyclodehydration.

In the case of the polymers, the temperatures k reaches the maximum value at are higher than for the models.

Table 5 Glass transition temperatures of the polymers before and after UV irradiation*

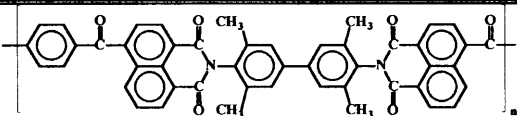
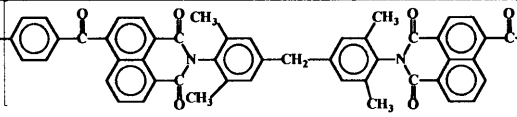
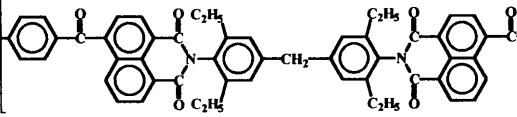
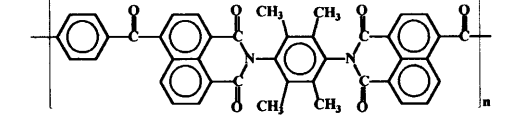
Structure	η_{red} [dl/g]	Tg (DSC, II run) [°C]	
		Before irradiation	After irradiation
	0.86	259	290
	0.66	265	280
	0.80	258	270
	0.58	245	260
*Mercury lamp 15 mW/cm ² , temp. 20°C, irradiation time 25 min			

Table 5 shows the glass transition temperatures of the polynaphthalimides before and after UV irradiation in HMPT solution at room temperature during 25 min. The polymers after irradiation were soluble in HMPT – no gelation process was observed but in all the cases the glass transition temperature increased in the range of 15–30°C in dependence on the diamine used for the polymer synthesis.

Acknowledgements The authors are grateful to the Scientific Research Committee (Warsaw, Poland) for support of this work (Grant No 3 709 B 075 14).

References

1. Sek D, Pijet P, Wanic A (1992) Polymer 33:190
2. Sek D, Wanic A, Schab-Balcerzak E (1995) J Polymer Sci Chem 33:547
3. Sek D, Wanic A, Schab-Balcerzak E (1997) J Polymer Sci Chem 35:539
4. Sek D, Wanic A, Janeczek H, Abadie MJM (1999) J Polymer Sci Chem 37:3523
5. Kanoaka Y, Kanoaka K (1972) Tetrahedron Lett 44:4517
6. Kanoaka Y (1978) Acc Chem Res 11:407