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High-temperature polycondensation of six membered dianhydrides with *o*-substituted aromatic diamines
1. Model compounds investigations

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Abstract

The high-temperature condensation of 4-benzoyl-1,8-naphthalene anhydride with 2,6-dimethylaniline and *o*-phenylenediamine was investigated. The structures of the compounds obtained were determined using FT-IR, UV–VIS, ^{13}C NMR, DSC and MS. The directions of reactivities of intermediate isoimides and imides were investigated. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

High-temperature condensation of six-membered anhydrides or dianhydrides with aromatic amines or diamines is used as a way of synthesis of six-membered imides or polyimides, respectively. These compounds are generally thermally and hydrolytically stable. However, when aromatic amines containing substituents in *ortho* position to amine group are used, there is the possibility of further reaction followed by the formation of a second, condensed five-membered ring. If in the reaction *o*-diamine is used, the final product has the aroylenebenzimidazole structure. The last reaction is applied for the synthesis of thermostable polyaroylenebenzimidazoles [1–3]. When *o*-alkylated amine is used, dehydrocyclization may take place, causing the formation of a pyrrole ring. This reaction is known for five-membered imides [4], but there is no information about similar reactions in the case of six-membered imide rings. Our previous investigations concerning the formation of six-membered imides confirmed that at the first step isoimide is formed instead of amic acid. At the next step the isomerization of isoimide to imide occurs [5]. In this work we present our results of investigation on the model reactions of six-membered anhydride with aromatic amines having substituents (methyl, amine) in *ortho* position to the nitrogen atom.

2. Experimental

2.1. Materials

2,6-Dimethylaniline (Aldrich) and isoquinoline (Aldrich) were distilled before use. *o*-Phenylenediamine (Fluka) was crystallized from the chloroform–cyclohexane mixture. Solvents were dried and purified in the usual manner.

2.2. 4-Benzoyl-1,8-naphthalene anhydride

4-Benzoyl-1,8-naphthalene anhydride was prepared by Friedel–Crafts acylation of acetonaphthene to 4-benzoyl-acenaphthene in chloroform followed by oxidation to diacid and cyclization to anhydride as described in [5].

2.3. Model compounds

2.3.1. Synthesis of N-(2,6-dimethylbenzene)-4-benzoyl-1,8-naphthalisoimides

4-Benzoyl-1,8-naphthalene anhydride (0.604 g, 2 mmol) and 2,6-dimethylaniline (0.242 g, 2 mmol) or its hydrochloride (0.315 g) in 10 ml of HMPT were placed in a container equipped with a magnetic stirrer, an air condenser, an inert gas inlet and heated at 180°C for 5 h. The product was precipitated with methanol, washed and dried in 100°C. When amine was used as a substrate *cis*-isoimide was formed, while using of amine hydrochloride caused the formation of *trans*-isoimide.

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2.3.2. Synthesis of N-(2,6-dimethylbenzene)-4-benzoyl-1,8-naphthalimide

To the reaction mixture of 4-benzoyl-1,8-naphthalene anhydride (2 mmol) and 2,6-dimethylaniline hydrochloride (2 mmol) in 10 ml of HMPT after 5 h of heating at 180°C, isoquinoline (0.258 g, 2 mmol) was added and the reaction was continued for another 5 h. The product was precipitated with methanol washed and dried at 100°C.

But, when the above reaction mixture after adding isoquinoline was heated at 180°C for an additional 18 h, two products were obtained. One of them was precipitated with methanol and was identified as *N*-(2,6-dimethylbenzene)-4-benzoyl-1,8-naphthalimide (yield 20%). The other was crystallized from the cooled solution after the separation of naphthalimide (yield 54%).

2.3.3. Synthesis of 4-benzoyl-1,8-naphthoylenebenzimidazol

4-Benzoyl-1,8-naphthalene anhydride (0.604 g, 2 mmol) and *o*-phenylenediamine (0.216 g, 2 mmol) in 10 ml of HMPT were placed in a container equipped with a magnetic stirrer, an air condenser and an inert gas inlet and were heated at 180°C for 4 h. The reaction mixture was poured into 150 ml of methanol. The resultant crystalline product after drying was extracted with chloroform. Two substances, soluble and insoluble in chloroform, were separated.

2.4. Measurements

Elemental analyses were carried out using a 240C Perkin–Elmer Apparatus. IR spectra were done on a Specord M80 spectrometer (resolution 2 cm^{-1}). Measurements were done in KBr pellets (concentration of about 0.2% w/w).

For the UV–VIS analyses, a Carl Zeiss Spectrometer was used. $CHCl_3$ was used as a solvent (concentration of about 1×10^{-4} mol/l).

^{13}C NMR spectra of investigated compounds were recorded on a Varian VXR 300 Spectrometer at 75 MHz resonance frequency using $CDCl_3$ as a solvent and TMS as an internal reference.

MS analyses were done on a SSQ 700 Finnigan Mat Mass Spectrometer using electron ionization of investigated samples.

^{15}N NMR spectra were done using Bruker Spectrometer. $CDCl_3$ was used as a solvent and TMS as an internal reference (with no nitrogen containing external reference).

Melting points were determined using Böetius Apparatus and confirmed by DSC technique (presented date mean the peak on DSC thermograms).

Thermal behaviour of the model compounds was investigated using DuPont 1090B Apparatus under argon atmosphere (flow rate about 4 ml/min) at the heating rate of 10 K/min (sealed aluminium pan, sample weight about 8 mg).

2.5. Characterization of the products

2.5.1. cis N-(2,6-dimethylbenzene)-4-benzoyl-1,8-naphthalisoimide

Yield 69.5%; elem. anal.: observed (calc.) C 79.91 (79.98)%, H 4.52 (4.72)%, N 3.56 (3.45)%; IR: 1708, 1667, 1365, 1273, 1243 cm^{-1}; UV–VIS: 344, 352 nm; MS: *m/e* = 405; DSC: m.p. 225°C; ^{15}N NMR: −189 ppm.

2.5.2. trans N-(2,6-dimethylbenzene)-4-benzoyl-1,8-naphthalisoimide

Yield 64,5%; elem. anal. observed (calc. as above) C 79.82%, H 4.67%, N 3.59%; IR: 1699, 1657, 1401, 1367, 1279, 1232 cm^{-1}; UV–VIS: 344, 352 nm; MS: *m/e* = 405; DSC: m.p. 193°C; ^{15}N NMR: −189 ppm.

2.5.3. N-(2,6-dimethylbenzene)-4-benzoyl-1,8-naphthalimide

Yield 74%; elem. anal. observed (calc.) C 79.94 (79.98)%, H 4.61 (4.72)%, N 3.54 (3.45)%; IR: 1672, 1636, 1400, 732 cm^{-1}; UV–VIS: 300 nm, MS: *m/e* = 405; DSC: m.p. 205°C; ^{15}N NMR: −276 ppm.

2.5.4. Product obtained after prolonged heating, crystallized from methanol after cooling

Yield 54%; elem. anal. observed (calc. for imide dehydration product) C 83.50 (83.70)%, H 4.30 (4.42)%, N 3.60 (3.55)%; IR: 1664, 1640, 1400 cm^{-1}, UV–VIS: 300 nm, MS: *m/e* = 387; DSC: m.p. 251°C.

2.5.5. Products obtained in the reaction of 4-benzoyl-1,8-naphthalene anhydride and o-phenylenediamine

- Product soluble in chloroform

  Yield 65.0%; elem. anal. observed (calc. for imidazol structure) C 79.85 (79.81)%, H 3.75 (3.89)%, N 6.18 (6.01)%; IR: 1701, 1692, 1664 cm^{-1}; UV–VIS: 300, 395 nm; DSC: m.p. 176°C.

- Product insoluble in chloroform

  Yield 4.8%; elem. anal. observed (calc. for amine–isoimid structure) C 76.68 (76.84)%, H 4.05 (4.16)%, N 5.63 (5.78)%; IR: 3356, 1708, 1664 cm^{-1}; UV–VIS: 344, 352 nm; DSC: m.p. 242°C.

3. Results and discussion

Our previous studies established that the high-temperature condensation of six-membered anhydrides and aromatic amines goes via isoimide as an intermediate instead of amic acid as it was expected generally. Depending on the presence or absence of the acidic catalyst, two different isomers of isoimides (*trans* or *cis*) can be formed. However, under the conditions of the high-temperature

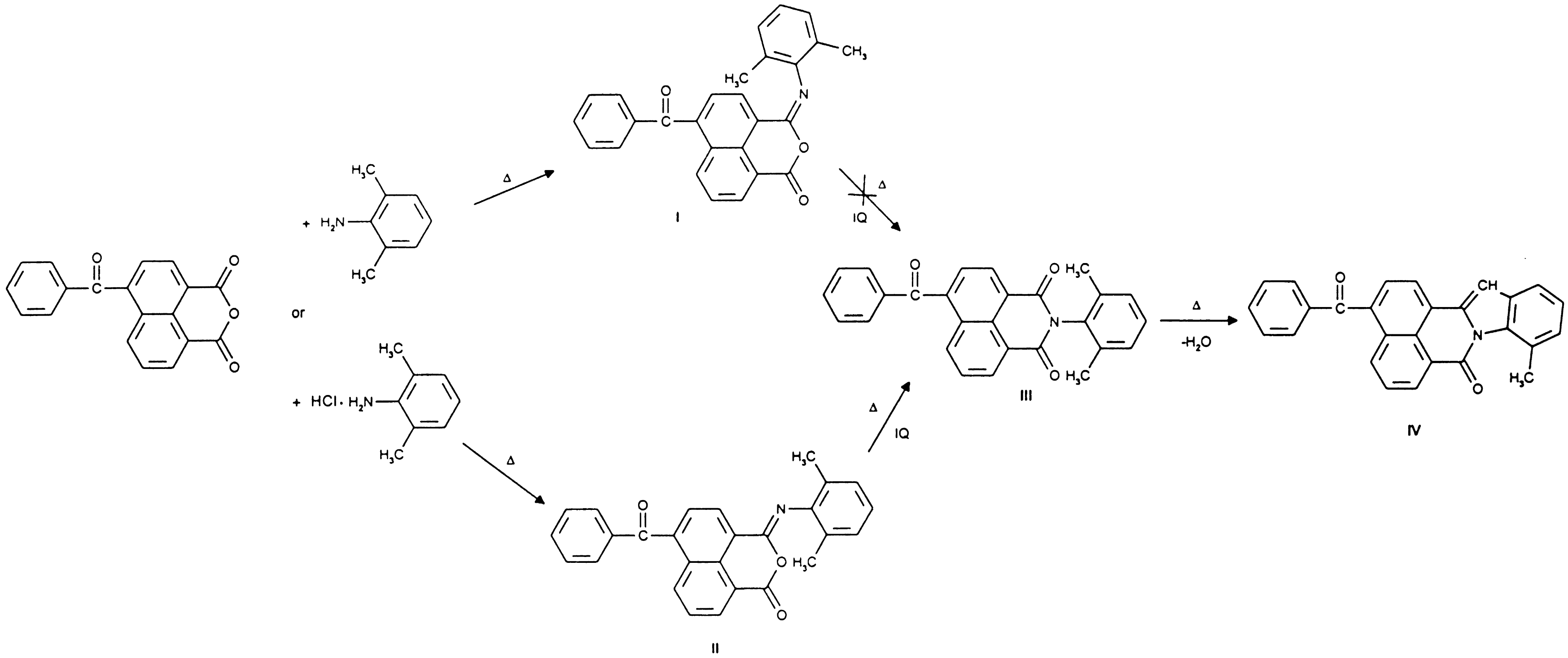
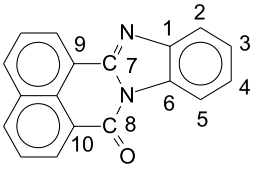


Fig. 1. Scheme of the high temperature condensation of 4-benzoyl-1,8-naphthalene anhydride with 2,6-dimethylanine.

Table 1
Calculated and observed chemical shifts

Carbon atom number	Chemical shifts (ppm)	
	Calculated	Observed
1	118.5	120.6
2	125.7	127.0
3	114.0	119.9
4	126.5	127.3
5	114.0	115.9
6	147.3	149.2
7		143.8
8		160.5
9		Overlapped
10		123.1
Structure		

condensation reaction, the rearrangement of only *trans*-isoimide to imide was observed. As the naphthalimides and polynaphthalimides obtained from aromatic amines, which do not contain substituents in *ortho* positions to amine group in aromatic rings, were almost insoluble in most organic solvents, we used in high temperature condensation the amine containing methyl substituents in these positions. The solubility of the model imide obtained from the 2,6-dimethylaniline strongly increased. But in this case we also observed the dehydrocyclization process as it was presented by Kanaoka [4] for the five membered imide ring (Fig. 1).

The reaction scheme presented in Fig. 1 was confirmed by identification of intermediate products (I), (II) and (III). Molecular masses of all these compounds, measured by MS, are equal to the value expected for both isoimides and imide ($m/e = 405$).

In the IR spectra of both isomeric isoimides, characteristic absorption bands for –COO– in six membered lactone rings (1708 cm^{-1} for *cis*-isoimide and 1699 cm^{-1} for *trans*-isoimide) and double –C=N– bond in imine (1668 cm^{-1} for the *cis* isomer and 1656 cm^{-1} for *trans* isomer) were observed. In both spectra the absorption bands attributed to six-membered lactone ether group at about 1200–1300 cm^{-1} were present.

Also UV spectra of these compounds, which exhibit the presence of absorption bands at 344 nm (–COO–) and 352 nm (–C=N–), confirm the isoimide structures.

However, both isomeric isoimides exhibited different melting points (225°C for the *cis* isomer, 193°C for the *trans* isomer), while m.p. of imide (III) is 205°C.

The IR spectrum of (III) is different from the IR spectra of isoimides. The main absorption band, which can be attributed to the six member imide carbonyl group was observed at 1636 cm^{-1} and no absorption of the six member lactone ether group at 1200–1300 cm^{-1} was observed.

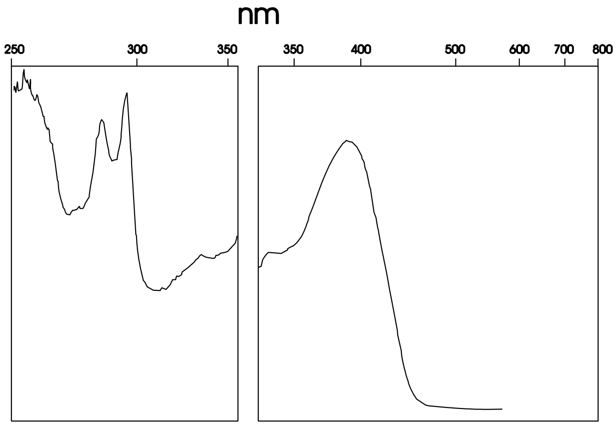


Fig. 2. UV–VIS spectrum of naphthoylenebenzimidazole.

Also the UV–VIS spectrum of (III) is completely different. The main absorption due to the six membered imide carbonyl group at ~300 nm was observed with no absorption above this value.

After prolonged heating of the substrates in the presence of isoquinoline added at the latter step of the reaction the product isolated (IV) exhibited a molecular mass of less than 18 than the previously described isoimides and imide ($m/e = 387$). It also exhibits a different melting point (251°C). This suggests that the dehydration occurred in this reaction.

The IR spectrum of compound (IV) is very similar to the IR spectrum of imide (III). The difference is that the main absorption due to the carbonyl group is slightly shifted to higher wavelengths (1644 cm^{-1} instead of 1636 cm^{-1}).

It should be pointed out that structure (IV) is similar to the naphthoylene-benzimidazole structure (see structure in Table 1) with the main difference in the presence of double C=C bond instead of double C=N present in naphthoylene-benzimidazole. When considering the ^{13}C NMR spectrum of naphthoylenebenzimidazole, the signal of carbon atom in ⟩C=N– structure was found at 143 ppm (Table 1).

In the ^{1}C NMR spectrum of the dehydrated compound three signals in the range 167.5–172.5 ppm were observed, which can be attributed to the six membered imide carbonyl carbon atom and two carbon atoms at the double C=C bond. The higher signal can be referred to the carbon atom, containing proton. No signal was observed at 143 ppm.

Fig. 2 presents the UV–VIS spectrum of naphthoylene-benzimidazole. The main absorption bands were found at ~300 nm (due to presence of the six membered imide carbonyl group) and 380 nm (due to presence of the double C=N bond).

In the UV spectrum of the product exhibiting the molecular mass 387, (Fig. 3), the absorption was observed at ~300 nm with no absorption above this value. This confirms the presence of six membered imide carbonyl and the absence of double C=N bond in this compound,

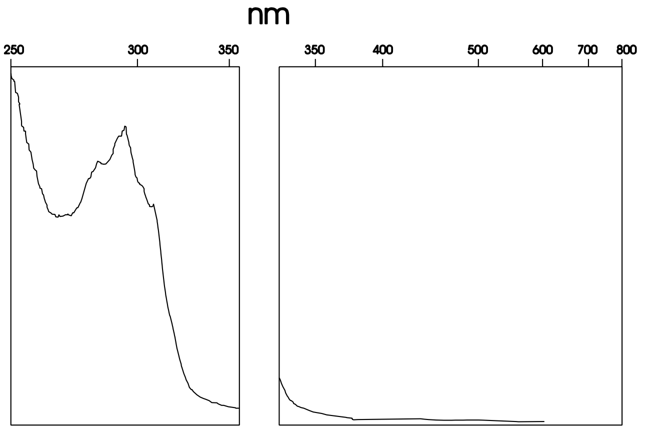


Fig. 3. UV–VIS spectrum of (IV).

and in this way confirms the structure (IV) for this compound.

Thus our investigations of high temperature condensation of six membered anhydrides with aromatic amines containing methyl substituents in *ortho* positions in amine aromatic rings confirms that the reaction goes via *trans*-isoimide and imide as intermediates to form the naphthoylenebenzopyrrole structure. We observed that the cyclodehydration process of imide to the pyrrole structure also proceeded under UV irradiation. The preliminary results confirm that the reaction under UV irradiation takes place at lower temperature and shorter time (the study there is in progress).

We expect that the condensation of six membered anhydrides with *o*-diamines due to naphthoylenebenzimidazole formation goes in the same way (Fig. 4).

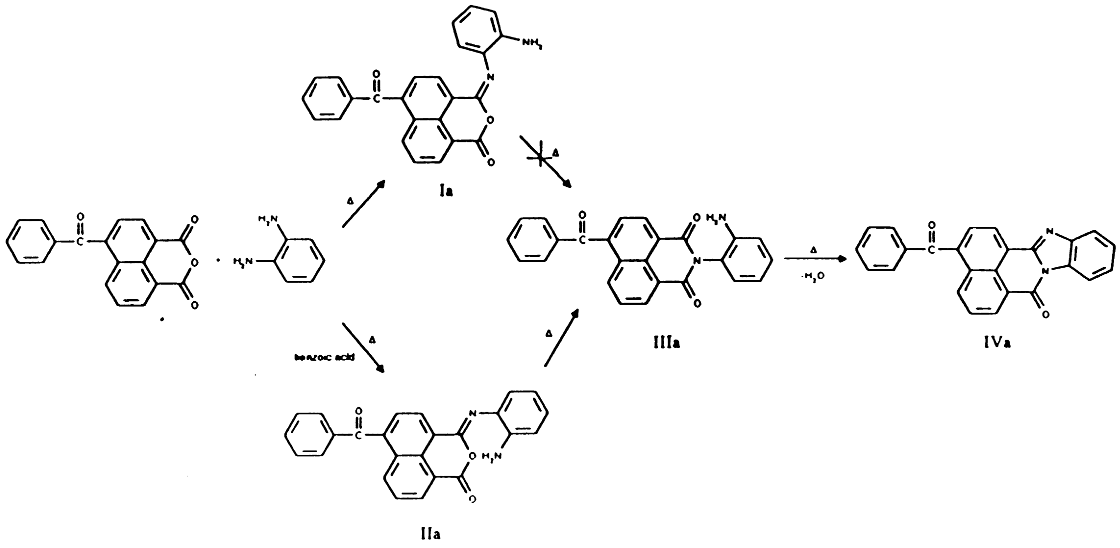


Fig. 4. Scheme of the high temperature condensation of 4-benzoyl-1,8-naphthalene anhydride with *o*-phenylenediamine.

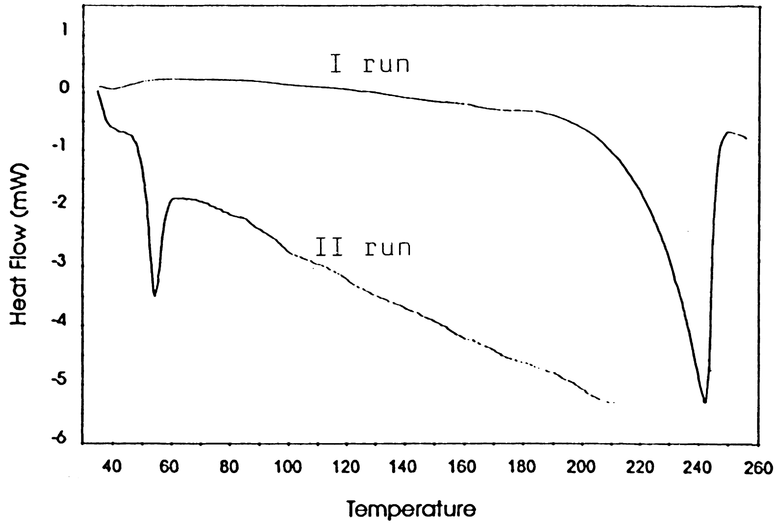


Fig. 5. DSC plot of (Ia).

However, due to faster isoimide–imide rearrangement for *trans*-isoimide obtained from *o*-phenylenediamine and higher reactivity of protons at the nitrogen atom towards carbonyl oxygen atom, products (IIa) and (IIIa) were not isolated. We managed to isolate product (Ia), containing free amine group (IR spectrum—absorption 3300–3600 cm^{-1} due to free and associated amine group, and 344 and 352 nm in UV–VIS: –COO– and –CN–, as described previously).

This compound seems to be a by-product of this reaction as it does not rearrange or dehydrate when heated. Fig. 5 presents two heating runs of product (Ia). When in the first run the melting point of isoimideamine was observed at 242°C, the second run exhibited the endotherm at 80°C, instead of the expected melting point of naphthoylenebenzimidazole (198°C). This confirms that melting of the compound (Ia) is accompanied with a destruction process.

4. Conclusion

Our study confirms that substituents (alkyl, amine) at the *ortho* position to the amine group do not change the mechanism of high temperature condensation of aromatic amines with 1,8 naphthalene type anhydride in comparison with the unsubstituted amines. In the first step of the reaction, whether *cis*- or *trans*-isomide is formed depends on the absence or presence of acidic catalyst. Only *trans*-isomide isomerizes to imide in the presence of a basic catalyst (isoquinoline). But when the substituent is an alkyl group with at least two hydrogens at the α-carbon, further reaction of the imide is possible and after dehydration a pyrrole ring is formed during heating or UV irradiation.

This intramolecular dehydrocyclization process of naphthalimides from *ortho*-alkyl substituted amines seems to be a new way for he synthesis a novel group of semiladder polymers—polynaphthoylbenzopyrroles.

Acknowledgements

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References

[1] Dawans F, Marvel CS. Polym Sci A 1965;3:3549.

[2] Arnold FE, van Densen RL. Polym Sci B 1968;6:815.

[3] Bower GM, Frost LW. Appl Polym Sci 1972;16:345.

[4] Kanaoka Y, Koyama K. Tetrahedron Lett 1972;44:4517.

[5] Sek D, Wanic A, Schab-Balcerzak E. Polym Sci Part A Polym Chem 1995;33:547.