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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Synthesis of Stereospecific Hinged Ladder Polyimides by Diels–Alder Reaction

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Abstract—A one-stage synthesis of hinge-ladder polyimides by Diels−Alder poly-condensation of polychlorinated cyclic bisimidodienes with bismaleimides containing aromatic and aliphatic groups was studied.

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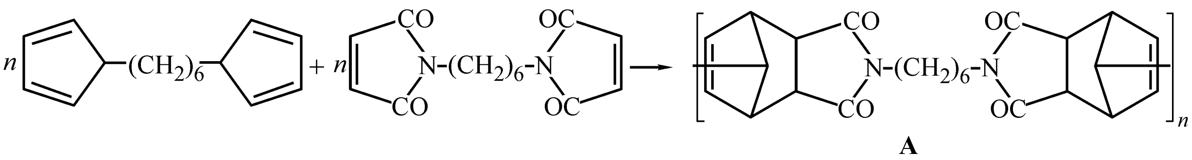
We know many methods of polyimide synthesis [1] however they are based mainly on the two-stage procedures [2] when the second stage is performed by the thermal way providing difficulties at determination of a dependence of a structure of amide fragments on polyimide properties. Besides the hinged polyimides obtained by the known methods do not possesses 100% imidization due to an incomplete conversion of the chain links of polyimide acids [1–3].

Polymerization by Diels–Alder (DA) reaction is one of promising trends in the preparation of polyimides of varios structures that promotes wide modification of the chemical composition and properties of the polyimides since both dienes of a cyclic structure and dienes with open chain can be applied to the reaction. In this case a bis-imide of unsaturated cyclic dicarboxylic acid, bis-maleimide, should be used as dienofil component.

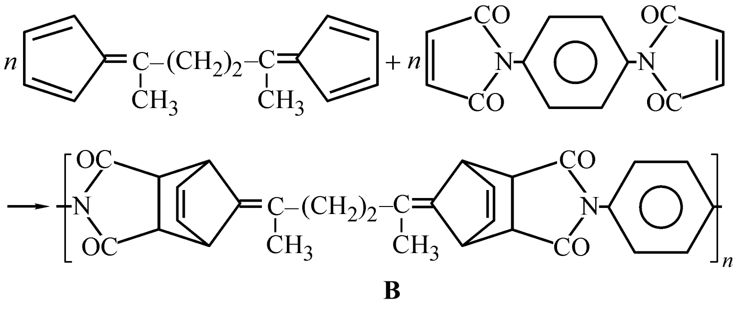
The synthesis of a polyimide (**A**) via DA polycondensation of bis-cyclopentadiene with *N,N'*-(hexamethylene)bismaleimide is reported in [4] (Scheme 1), and bis-fulvene with bis-maleimide in DMF at 60–70°C according to Scheme 2 resulted in polyimide (**B**) preparation as described in [5].

DA polymerization is important at designing oriented ladder molecules. However available studies in this field do not make clear the idea of a spatial structure

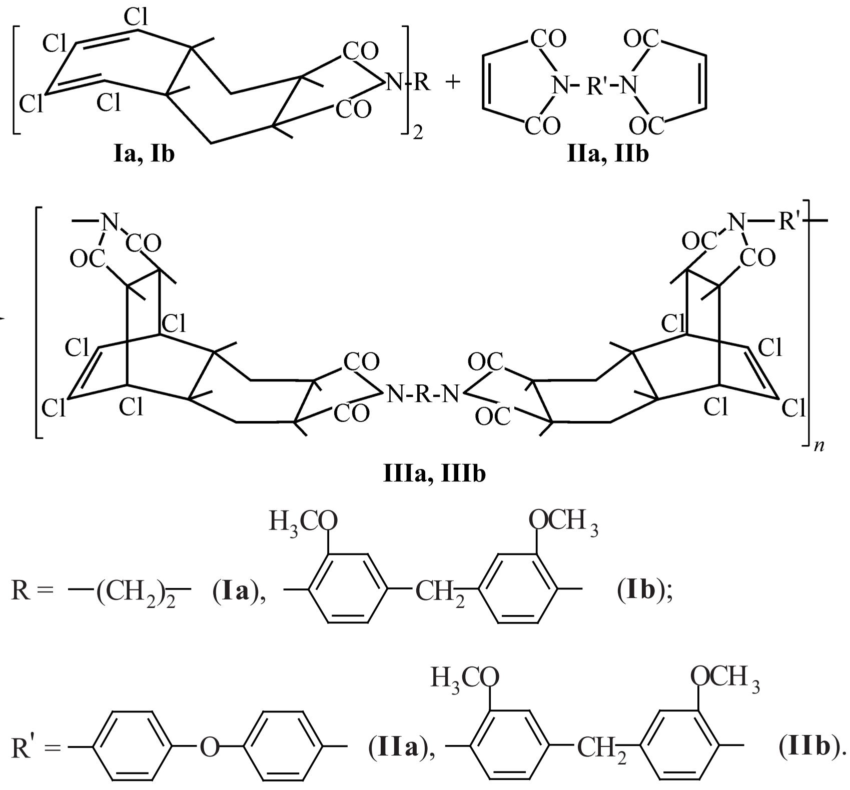
Scheme 1.



Scheme 2.



Scheme 3.



of the prepared polyimides that firstly is caused by an absence of proper bis-dienes, whose stereochemistry can be unambiguously determine the configuration of the polymer chain fragments [6]. And secondly data about application of DA polycondensation to halogen-containing polyimides is absent in literature. Thus in this paper we suggest one-stage synthesis of hinged ladder polyimides of desired spatial structure by DA reaction of chlorinated bis-cyclic bis-imidodienes (**Ia, Ib**) of known spatial structure with bis-maleimides (**IIa, IIb**) that gives hinged ladder fragments of *endo* and *exo* configurations. In the course of this reaction an formation of side low-polymeric products is not observed as in the course of an usual polycondensation and that is an advantage of this method.

The synthesis of the polyimides was conducted by one-stage DA reaction of *N,N'*-(1,2-ehtane)bisimide (**Ia**) or *N,N'*-(3,3'-dimethoxy-4,4'-diphenylmethane)bisimide of *endo*,*exo*-2,3,4,5-tetrachlorobicyclo[4.4.0]deca-2,4-dien-8,9-dicarboxylic acid (**Ib**) with bismaleimides (**IIa, IIb**) according to Scheme 3.

DA polycondensation was performed in high-polar solutions (DMAA, and DMF) that provide homogeneity of reaction medium, and 100% polycondensation in the presence of a small quantity of hydroquinone at 150°C for 6–7 hours due to a good solvating power of initial monomers and produced polyimides.

The obtained polychlorinated ladder polyimides (**IIIa–IIId**) are solid products. Their composition and structure are confirmed by the data of elemental analysis, and IR spectroscopy, and also by an authentic synthesis.

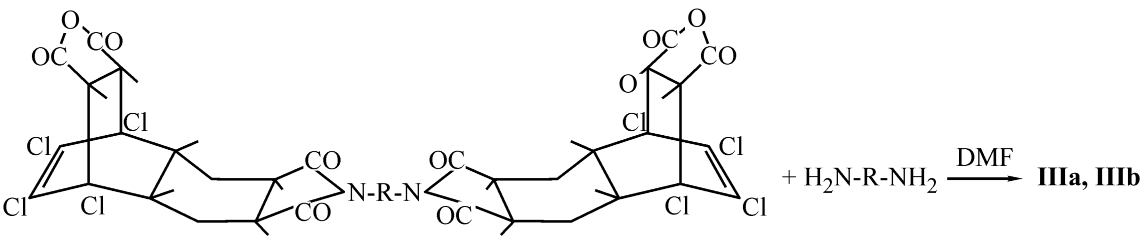
The IR spectra of the polyimides **IIIa–IIId** contain absorption bands at 1720 and 1780 cm^{-1} (C=O), 1601 cm^{-1} (C=C), and 680–720 cm^{-1} (C–Cl).

The authentic synthesis of the polyimides **IIIa–IIId** was performed by diacylation of an apropriate diamine with bis-imidodianhydride (**IVa, IVb**) of known spatial structure in DMF according to Scheme 4, where R and R' are substituents noted above.

Characteristics of the polyimides **IIIa–IIId** obtained by both methods completely coincide. TG and DTA indicate (Fig. 1) that the polyimides **IIIa–IIId** are thermoresistant, their destruction starts at 300–350°C, and at 360–400°C they lose only 10% of an initial weight.

The DA polycondensation is fully stereo-specific course forming the polyimides in whose ladder maleimide and cyclohexane rings are of *endo,endo*

Scheme 4.



IVa, IVb

configuration relative to a rigid bicyclooctane fragment.

EXPERIMENT

IR spectra of the synthesized compounds were recorded on a spectrometer UR-20. Samples were prepared in a liquid paraffin. A purity was checked by thin-layer chromatography using benzene–dichloroethane–acetic acid (8 : 3 : 1.5, by volume) as eluent, spots were detected under UV light [7].

Thermoresistance measurements was performed by TGA and DTA methods on a MOM instrument (Hungery).

Reduced viscosity [η] of 0.5% polyimides solution was measured on Ubbelohde instrument at 25°C in dimethylformamide.

***N,N'*-(4,4'-Diphenyl(oxide)bismaleimide (IIa)** was synthesized by reaction 4,4'-diaminodiphenyloxyde with maleic anhydride in diethyl ester medium with subsequent cyclization of the formed amido acid in the acetic anhydride in the presence of pyridine according to [8]. Yield 92%, mp 183–185°C. Found, %: C 66.2, H 2.91, N 7.3. $C_{20}H_{12}N_2O_5$. Calculated, %: C 66.7, H 3.39, N 7.8.

***N,N'*-(3,3'-Dimethoxy-4,4'-diphenylmethane)bismaleimide (IIb)** was synthesized analogously. Yield 90.6%, mp 156–158°C. Found, %: C 66.0, H 4.3, N 6.7. $C_{23}H_{18}N_2O_6$. Calculated, %: C 65.7, H 3.89, N 6.3.

***N,N'*-(1,2-Ethane)bisimide *endo,exo*-2,3,4,5-tetrachlorobicyclo[4.4.0]deca-2,4-dien-8,9-dicarboxylic acid (Ia)** was synthesized by method described in [9]. Yield 80%, mp 223–224°C (chloroform–hexane). Found, %: C 44.21, H 2.77, Cl 40.18, N 3.78. $C_{26}H_{20}Cl_8N_2O_4$. Calculated, %: C 44.06, H 2.82, Cl 40.11, N 3.95. IR spectrum, cm^{-1}: 1710, 1770 (C=O), 1605 (C=C), 670–750 (C–Cl).

***N,N'*-(3,3'-Dimethoxy-4,4'-diphenylmethane)-bisimide *endo,exo*-2,3,4,5-tetrachlorobicyclo[4.4.0]-deca-2,4-diene-8.9-dicarboxylic acid (Ib)** was synthesized by method [9]. Yield 90%, mp 293–295°C (chloroform–hexane). Found, %: C 60.15, H 3.29, Cl 30.78, N 3.02. $C_{39}H_{30}Cl_8N_2O_4$. Calculated, %: C 61.65, H 3.31, Cl 31.34, N 3.09. IR spectrum, cm^{-1}: 1715, 1780 (C=O), 1605 (C=C), 670–750 (C–Cl).

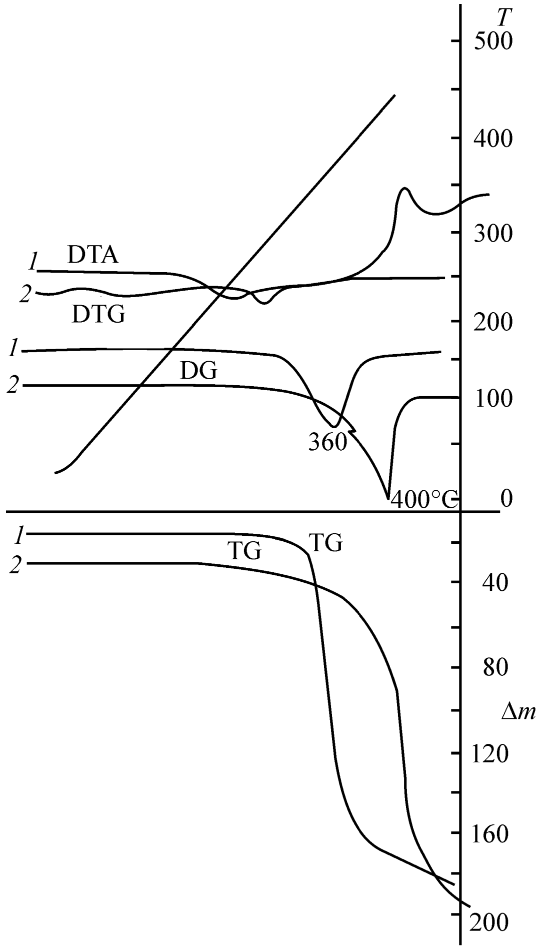


Fig. 1. DTA and TG curves of the polyimides **IIIa** (*1*) and **IIId** (*2*). (Δ*m*) loss of weight, %, (*T*) temperature, °C.

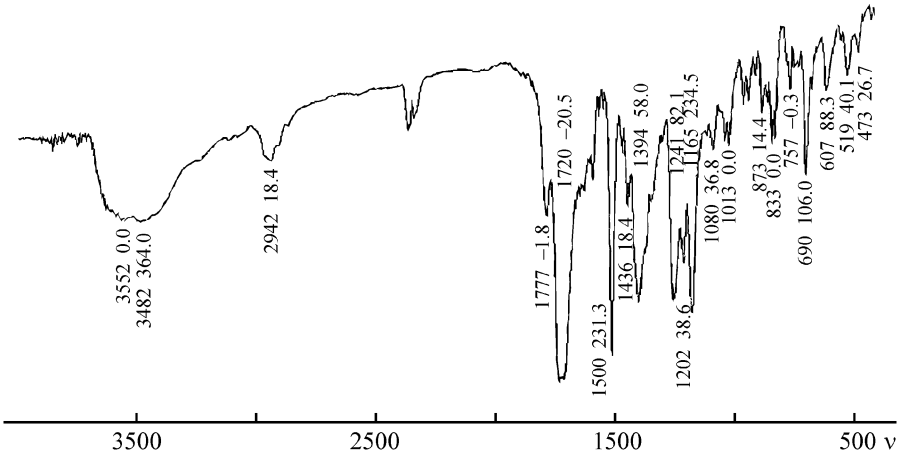


Fig. 2. IR spectra of the polyimide **IIIa** on the basis of *N,N'*-(1,2-ethane)bisimide *endo,exo*-2,3,4,5-tetrachlorobicyclo[4.4.0]-deca-2,4-dien-8,9-dicarboxylic acid and of *N,N'*-(4,4'-diphenyloxyde)bismaleimide. Transmission, %, (ν) wave number cm^{-1}.

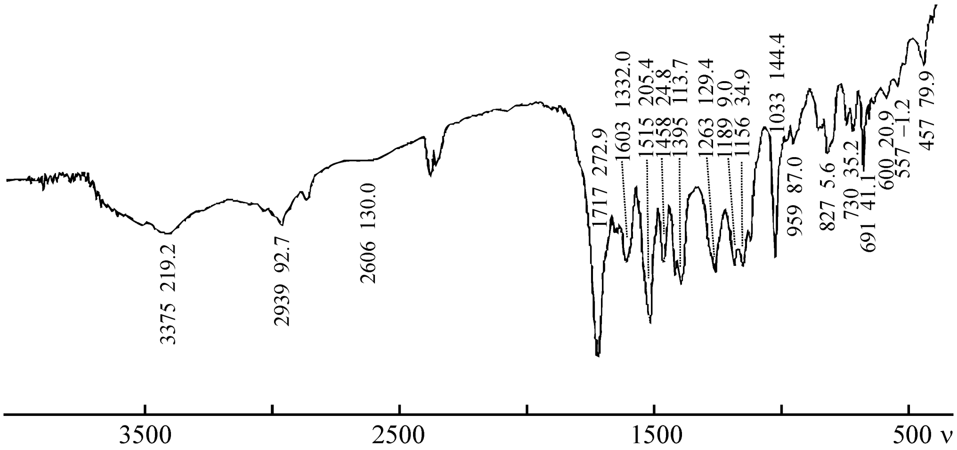


Fig. 3. IR spectra of the polyimide **IIId** on the basis of *N,N'*-(3,3'-Dimethoxy-4,4'-diphenylmethane)bisimide *endo,exo*-2,3,4,5-tetrachlorobicyclo[4.4.0]-deca-2,4-diene-8.9-dicarboxylic acid and of *N,N'*-(3,3'-dimethoxy-4,4'-diphenylmethane)bis-maleimide. Transmission, %, (ν) wave number cm^{-1}.

Dianhydrides of *endo,endo,endo*-2,3,4,5-tetrachlorotricyclo[6.2.1.0^{5,10}]dodec-2-en-7,8-dicarboxyimide-11,11,12,12-tetracarboxylic acid (IVa, IVb) was synthesized by method [10]. 10 mmol of *N,N'*-(1,2-ethane)- (**IVa**) or *N,N'*-(3,3'-dimethoxy-4,4'-diphenylmethane)bisimide *endo,exo*-tetrachlorobicyclo[4.4.0]-deca-2,4-dien-8,9-dicarboxylic acid (**IVb**) and excess (15–20 g) of the maleic anhydride was heated at 160°C for 4–6 h. Then this mixture was poured into chloroform. The separated crystals were filtered off, washed with chloroform and recrystallized from a mixture benzene–acetone. Yield (**IVa**) 90%, mp 302°C. Found, %: C 44.80, H 2.51, Cl 31.25, N 2.84. $C_{34}H_{24}Cl_8N_2O_{10}$. Calculated, %: C 45.13, H 2.65, Cl 31.42, N 3.09. Yield (**IVb**) 92%, mp 302°C. Found, %: C 50.91, H 2.99, Cl 25.61, N 2.11. $C_{47}H_{34}Cl_8N_2O_{12}$. Calculated, %: C 51.18, H 3.08, Cl 25.77, N 2.54. IR spectrum, cm^{-1}: 1715, 1780 (C=O), 1605 (C=C), 670–750 (C–Cl).

In 3.54 g (0.005 mol) of *N,N'*-(1,2-ethane)bisimide *endo,exo*-2,3,4,5-tetrachlorobicyclo[4.4.0]deca-2,4-dien-8,9-dicarboxylic acid (**Ia**) 1.8 g (0.005 mol) of *N,N'*-(4,4'-diphenyloxyde)bismaleimide (**IIa**), 0.05 g of hydroquinone and 16 g of absolute dimethylacetamide were dissolved in a dry three-neck flask equipped with a stirrer, a thermometer and a reflux cooler with calcium chloride tube. Concentration of initial components in the reactive mixture is 25 wt %. A content of the flask was stirred at 150°C for 6 h. The reactive mixture was poured into ice water. The separated powder product was filtered off, washed with water, and then with methanol, and dried at 60°C. Yield (**IIIa**) 4.9 g (92%). Characteristic viscosity [η] = 0.28 dl g^{-1} (0.5% dimethylformamide, 25°C). Found, %: C 51.02, H 2.92, Cl 26.15, N 5.04. $C_{46}H_{32}Cl_6N_4O_9$ (1:1). Calculated, %: C 51.69, H 3.00, Cl 26.59, N 5.24. IR spectrum, cm^{-1}: 1710, 1785 (C=O), 1605 (C=C), 670–750 (C–Cl) (Fig. 2).

Polyimide **IIIb**, 3.54 g (0.005 mol), was obtained like the previous experiment from 3.54 g (0.005 mol) of amidobisdiene (**Ia**) and of 2.09 g (0.005 mol) of *N,N*'-(3,3'-dimethoxy-4,4'-diphenylmethane)bismaleimide (**IIb**) at concentration of initial monomers of 25 wt %. Characteristic viscosity [η] = 0.32 dl g^{-1} (dimethylformamide, 25°C). Found, %: C 52.00, H 2.89, Cl 24.91, N 4.59. $C_{49}H_{38}Cl_8N_4O_{10}$ (1:1). Calculated, %: C 52.22, H 3.37, Cl 25.22, N 4.97. IR spectrum, cm^{-1}: 1708, 1780 (C=O), 1603 (C=C), 650–750 (C–Cl).

Polyimide **IIIc,** 4.47 g (92%), [η] = 0.35 dl g^{-1}, was obtained like the first experiment from 6.33 g (0.005 mol) of *N,N*'-(3,3'-domethoxy-4,4'-diphenylmethane)bisimide *endo,exo*-2,3,4,5-tetrachloro-bicyclo[4.4.0]deca-2,4-dien-8,9-dicarboxylic acid (**Ib**) and 1.8 g (0.005 mol) of *N,N*'-(4,4'-diphenyloxide)bis-maleimide (**IIa**) at concentration of initial monomers of 25 wt % in dimethylformamide medium. Found, %: C 55.55, H 3.00, Cl 21.99, N 4.02. $C_{59}H_{42}Cl_6N_4O_{11}$ (1:1). Calculated, %: C 55.92, H 3.32, Cl 22.49, N 4.42. IR spectrum, cm^{-1}: 1710, 1785 (C=O), 1605 (C=C), 670–750 (C–Cl).

Polyimide **IIId**, 8.20 g (94%), [η] = 0.36 dl g^{-1} was synthesized like the first experinment from 6.33 g (0.005 mol) of bisimidodiene (**Ib**) and 2.09 g (0.005 mol) of *N,N* '-(3,3'-domethoxy-4,4'-diphenylmethane)bismale-imide (**IIb**) at concentration of initial monomers of 25 wt % in DMAA medium. Found, %: C 55.88, H 3.49, Cl 21.11, N 3.96. $C_{62}H_{51}Cl_8N_4O_{12}$ (1:1). Calculated, %: C 56.02, H 3.84, Cl 21.38, N 4.21. IR spectrum, cm^{-1}: 1708, 1780 (C=O), 1603 (C=C), 650–750 (C–Cl) (Fig. 3).

CONCLUSIONS

(1) The one-stage synthesis of the hinge-ladder polyimides by the Diels–Alder polycondensation of polychlorinated bis-imidodienes with bis-maleimides was developed.

(2) The structure of the synthesized polyimides was established by IR spectra and the authentic synthesis.

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