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Star-Shaped Poly((9-carbazolyl)methylthiirane): A New Polymer for Optoelectronic Applications

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Summary: The polymerization of (9-carbazolyl)methylthiirane in the presence of cyclic oligo(potassium glycidoxide) as the macroinitiator activated 18-crown-6 leads to polythioether with the molecular masses relatively near to the calculated ones. This polythioether dispersed in a commercially available transparent polymer gives a new blue photoluminescent material.

Introduction

Information about carbazolyl-containing polythioethers were till now rather limited. It was mainly showed that their synthesis in the presence of cationic or anionic initiators resulted in low-molecular products, which revealed photoluminescence properties.[1]

More data could be found in the literature on the synthesis of carbazolyl-containing polyethers. Potassium hydroxide was firstly used for the polymerization of (9-carbazolyl)methyloxirane (CMO) at 120 °C[2] DP_n of the polymer ranged from 8 to 12. The addition of 18-crown-6 to the reaction mixture allowed to conduct the polymerization at lower temperature.[3]

Polyethers with higher molecular masses were obtained when potassium hydride was applied as the initiator.[4] For example, poly((2-(9-carbazolyl)ethoxymethyl)oxirane) had DP_n of ca. 60, but the polymerization of CMO resulted still in low-molecular products. Study on the initiation step of 2-(9-carbazolyl)ethyl glycidyl ether polymerization by alkalide K^-, K^+ (15-crown-5)$_2$ were also presented.[5]

Then, an idea was proposed how to get poly(CMO) of relatively high molecular masses.[6] It was based on the use of cyclic oligo(potassium glycidoxide) as a macroinitiator with mainly six active centers,[7] which has been already known to give star-shaped polyethers.[8] However, that way turned out to be unsuccessful. The reason for that was a proton transfer which occurred during the anionic polymerization of CMO. That side reaction resulted in deactivation of the initiator and in the formation of a mixture of star-shaped and linear macromolecules. All the macromolecules had the hydroxyl end groups instead of the expected methoxy ones.

Despite of the fact that poly(CMO) had low-molecular masses and irregular structure, it showed quite good photoluminescence properties. Therefore, a similar monomer, i.e. (9-carbazolyl)methylthiirane (CMT), was selected for the further study and in this work we discuss their preliminary results.

Experimental Part

Analyses

Number–average molecular masses and dispersities of poly(CMT) were estimated by the use of size exclusion chromatography technique on a Shimadzu instrument equipped with SEC Phenomenex column 500 Å. Tetrahydrofuran was used as a solvent with flow rate on the level of 1 cm^3/min at 40 °C. Poly(ethylene oxide) standards of low dispersity were applied to generate a calibration curve.

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Gas chromatography–mass spectrometry (GC-MS) analyses were run on a 5-m long pre-column and 30-m long fused 5%phenyl 95%dimethylpolysiloxane ZB-5MSi capillary column, using a Shimadzu QP2010plus gas chromatograph.

Luminescencespectrawere obtained on a Jobin-Yvon spectrofluorymeter FLUOROMAX-4 with the 150 W xenon lamp as a ion source. Spectra were measured at 20 °C with the resolution of 0.1 nm without smoothing and correction.

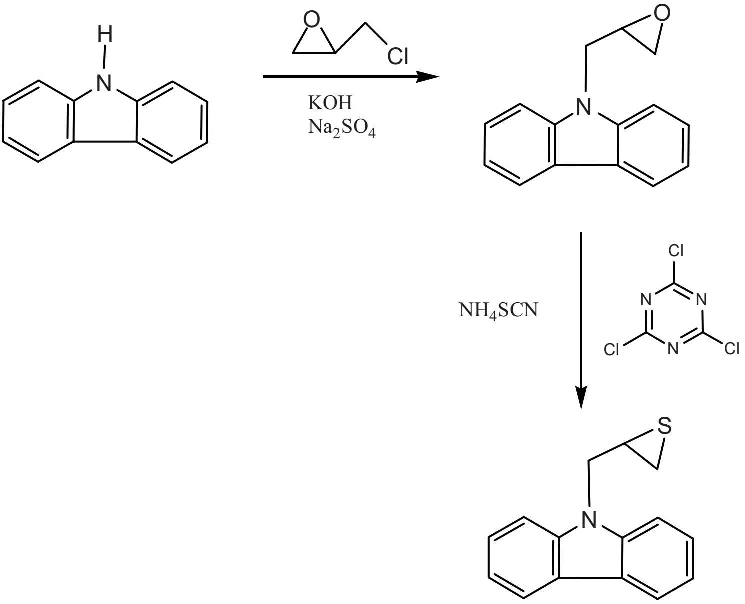
Syntheses

All syntheses were carried out at 20 °C in a 50 cm^3 reactor equipped with a magnetic stirrer and teflon valves enabling substrates delivery and sampling under argon atmosphere.

The monomer was synthesized in two steps (Scheme 1).[9] In the first step the reaction of 9*H*-carbazole (1.5 g, 8.97 mmol) with 2-(chloromethyl)oxirane (0.83 g, 8.97 mmol) in the presence of KOH (1.5 g, 26.78 mmol) and Na_2SO_4 (0.63 g, 4.44 mmol) resulted in (9-carbazolyl)-methyloxirane (1 g, 4.48 mmol).

In the second step (9-carbazolyl)methyloxirane (1 g, 4.48 mmol) was treated with 2,4,6-trichloro-1,3,5-triazine (0.016 g, 0.087 mmol) and ammonium thiocyanate (0.68 g, 8.93 mmol) in tetrahydrofuran (20 cm^3). The product was purified on the chromatographic column filled with silica gel and using a mixture of acetone with hexane (1:3 vol.) as an eluent. The yield of (9-carbazolyl)methylthiirane was equal to 42% (0.45 g) and m.p. 100–101 °C.

In one experiment oligo(potassium glycidoxide) was prepared in the reaction of glycidol (0.022 g, 0.37 mmol) with potassium hydride (0.015 g, 0.37 mmol) and 18-crown-6 0.1 g, 0.37 mmol) in tetrahydrofuran (15 cm^3).[7] Then, (9-carbazolyl)-methylthiirane (CMT) (5.3 g, 22.2 mmol) dissolved in tetrahydrofuran (10 cm^3) was added to the reactor while mixing. The changes of monomer concentration were monitored by gas chromatography - mass spectrometry technique. Finally, alkoxide active centers were transformed into the methoxy end groups by the addition of methyl iodide (0.5 cm^3). A crown ether complex with potassium iodide was filtered off and the residual solution was treated with methanol (20 cm^3). The precipitated polymer was dried at elevated temperature



Scheme 1.
Synthesis of (9-Carbazolyl)methylthiirane.

under vacuum giving 4.3 g of poly(CMT) (yield 81.3%).

Tetrahydrofuran solutions of poly(CMT) were prepared in the concentration range of 10^{-4}-10^{-7} mol/dm^3.

In another series of experiments poly(CMT) was dispersed in commercially available transparent polymers (CAP)s, i.e. in polycarbonate, polystyrene or poly(methyl methacrylate). In this case poly(CMT) (0.1 g) with the selected CAP (10 g) were dissolved in chloroform (200 cm^3) and thin films were prepared from the solutions obtained.

Results and Discussion

Poly(CMT) obtained at various monomer and macroinitiator concentrations has molecular masses relatively close to the calculated ones (Table 1). Therefore, it can be assumed that this polymer has a regular structure and its macromolecules are built from a cyclic crown-like core and mainly six arms.[8]

Poly(CMT) dissolved in tetrahydrofuran reveals blue photoluminescence and its intensity depends on the polymer concentration. This dependence has a maximum at the polymer concentration of 2×10^{-6} mol/dm^3 (Figure 1), whereas in the case of poly(CMO) the maximum was observed at 5×10^{-5} mol/dm^3.[6]

Commercially available transparent polymers (CAP)s, i.e. polycarbonate, polystyrene and poly(methyl methacrylate) were then applied instead of the solvent for the preparation of photoluminescent polymer materials.

Table 1.
Molecular masses and dispersities of poly(CMT).

No.	Initial monomer concentration $[M]_o$, mol/dm^3	Initiator concentration $[I]_o$, mol/dm^3	Molecular mass calculated $^{x/}$ $M_{n\ calc}$	Molecular mass estimated (SEC) M_n	Dispersity (SEC) M_w/M_n
1	0.54	0.022	5 900	6 500	1.25
2	1.76	0.037	11 400	9 300	1.22
3	1.85	0.031	14 300	12 000	1.30

$^{x/}$Mn calc = 239 $[M]_o/[I]_o$

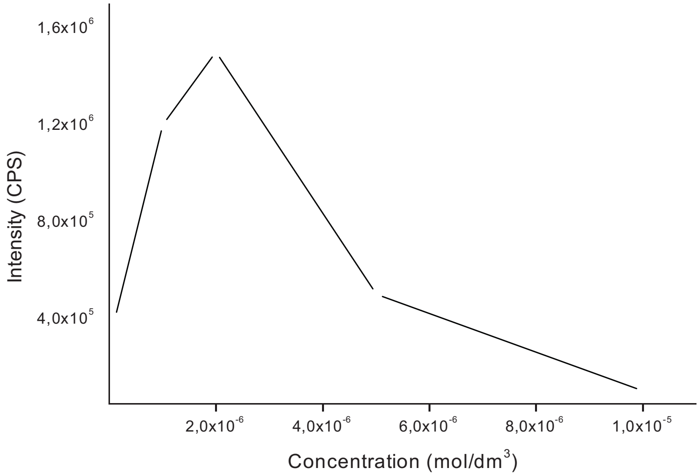


Figure 1.
Dependence of the intensity of poly(CMT) photoluminescence on its concentration in tetrahydrofuran solution at 20 °C.

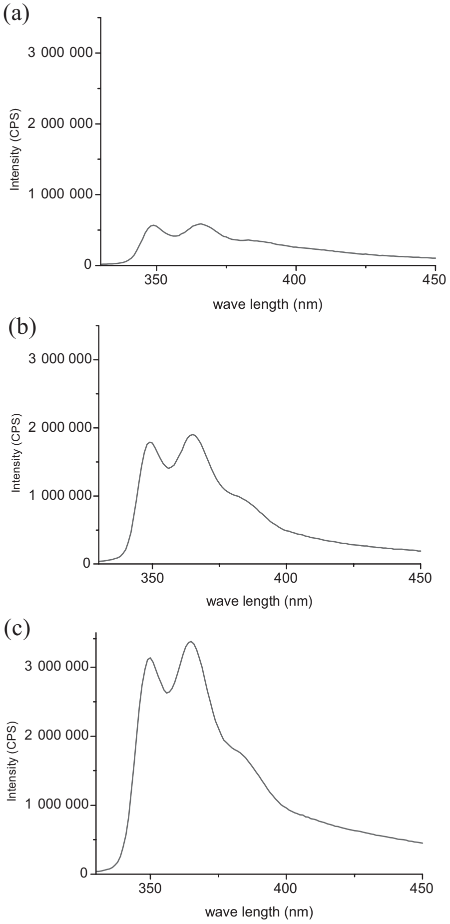


Figure 2.
Emission spectra of thin films prepared from poly(CMT) and polycarbonate (a), polystyrene (b) and poly(methyl methacrylate) (c) in a weight ratio 1:100, respectively, excited with wave length 295 nm.

The analysis of thin films prepared from CAP and poly(CMT) shows that the highest intensity of photoluminescence reveals poly(CMT) dispersed in poly(methyl methacrylate) (Figure 2). A kind of CAP does not influence the emission wave length.

It seems that this material can be proposed for the construction of Organic Light Emitting Devices (OLED)s or for the others optoelectronic applications.

Conclusions

Polythioether with molecular masses close to the calculated ones was synthesized from (9-carbazolyl)methylthiirane using cyclic oligo(potassium glycidoxide) as the macroinitiator. The intensity of its photoluminescence in tetrahydrofuran solution changed with the polymer concentration. A new photoluminescent material was obtained when the solvent was replaced with a common available transparent polymer. A particularly intensive blue photoluminescence revealed poly((9-carbazolyl)-methylthiirane) dispersed in poly(methyl methacrylate).

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