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Synthesis and Polymerization of 2-(β-N-Carbazolylethyl)-2-Oxazoline and 2-(3,5-Dinitrophenyl)-2-Oxazoline

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SUMMARY

The synthesis of 2-(β-N-carbazolylethyl)-2-oxazoline, 2-(3,5-dinitrophenyl)-2-oxazoline and of their cationic living ring opening isomerization polymerization in the presence of methyl p-toluenesulfonate are described.

INTRODUCTION

Continuing the interest in monomers and polymers with electrono-donor and electrono-acceptor aromatic substituents[1,2] and in inter- and intramolecular macromolecular charge transfer complexes[3,4], this paper will present the synthesis of two new cyclic imino ethers containing electrono-donor or electrono-acceptor substituents.

The polymerization of cyclic imino ethers has been known only since the last 15 years, and has now become a quite active field of investigations[5]. Cationic polymerization of 2-oxazolines proceeds via the ring opening involving isomerization to produce poly(N-acylethylenimine). In a few cases the polymerization takes place through a living mechanism. In these conditions, 2-substituted 2-oxazolines seems to be the only class of monomers containing electrono-donor or electrono-acceptor groups able to polymerize through a living mechanism.

In some previous papers, we have shown that thermal reversible networks can be obtained both through intra- or intermolecular charge transfer interactions[6,7]. The matching effect (i.e., the length of the main chain repeating units separating pendant donor or acceptor groups, the distance between each other pendant groups, and the polymer molecular weight) is very important in the design of such thermal reversible networks. If the distance between the main chain and the donor or acceptor group can be very simply changed in the case of acrylate or methacrylate type monomers, the distance between each other pendant group can be varied through polymerization of cyclic imino ethers having different heterocyclic ring size.

On this account, the present paper will present the synthesis of 2-(β-N-carbazolylethyl)-2-oxazoline (CEOxz), 2-(3,5-dinitrophenyl)-2-oxazoline (DNPhOxz) and preliminary data on their

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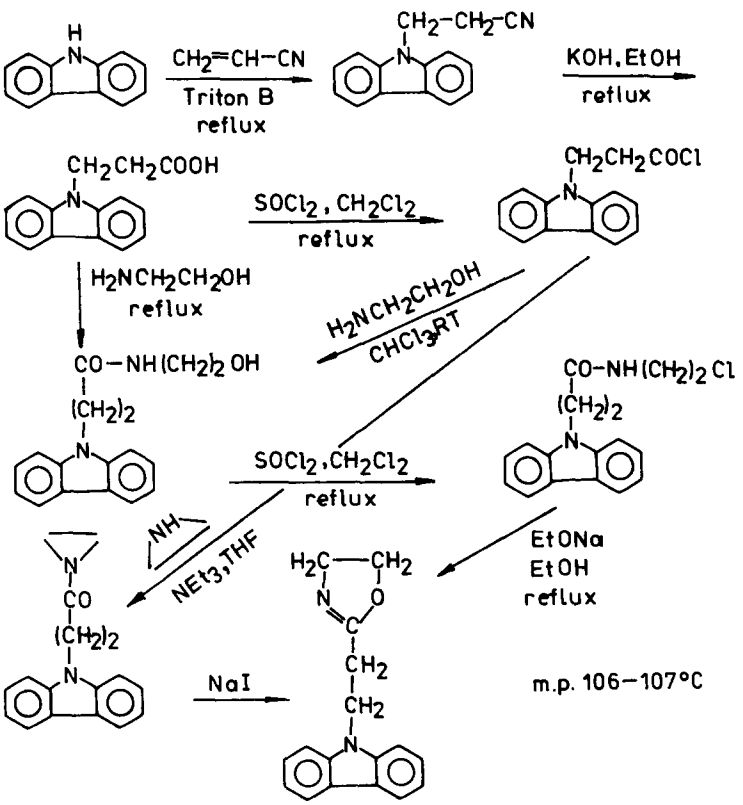
cationic living polymerization. The polymerization of these monomers leads to polymers containing pendant groups having donor or acceptor character separated by two methylene groups.

EXPERIMENTAL AND RESULTS

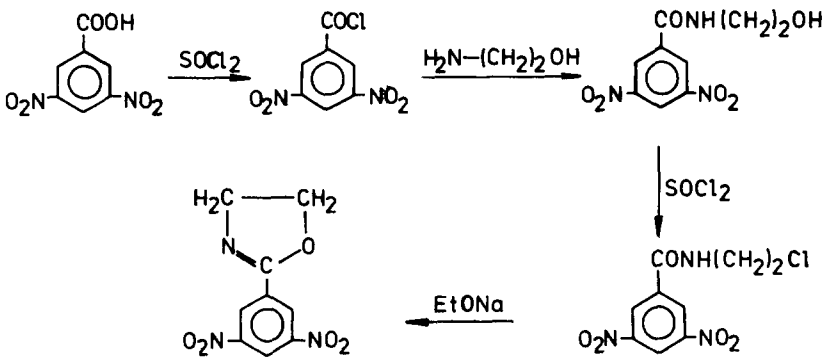
The elemental analysis results of synthesized compounds are in agreement with theoretical values, therefore they will not be presented. Infrared (IR) spectra were recorded on a Perkin-Elmer 577 spectrophotometer (KBr pellets) and NMR spectra on a JEOL (60-MHz) instrument. DMF was dried over 4A molecular sieves and then distilled under argon. Methyl p-toluenesulfonate was synthesized by esterification of tosylchloride with methanol, and purified through several distillations under argon. The monomers were synthesized according to the reactions in Scheme 1 and 2. Some possibilities for the synthesis of CEOxz were used. Between them the most suitable is presented.



Scheme 1.

2-(N-carbazolyl)propionitrile.
It was synthesized through the cyanoethylation of carbazole (167g, 1.0 mole) with acrylonitrile in the presence of 4ml benzyltrimethylammonium hydroxide (Triton B) (40% methanol solu-

tion) as catalyst[8]. After recrystallization from acetone the yield was 80% (176.22g). m.p. 155.5°C. IR(KBr):2240 (νC=N), 744, 720 cm^{-1} (νCH aromatic). NMR($(CD_3)_2CO$,σ, ppm): 3.02 (t,CH_2CN), 4.61 (t, NCH_2), 6.9-7.6 (m, 6 aromatic protons), 8.04 (d, 2 aromatic protons).



Scheme 2.

2-(N-carbazolyl)propionic acid.
It was obtained by hydrolysis of 2-(N-carbazolyl)propionitrile. A mixture of 146g (0.66 mole) 2-(N-carbazolyl)propionitrile, 2000 ml ethanol, 372g KOH and 1000 ml water was stirred at reflux temperature until all reaction mass was dissolved (ca. 3 hours). The solution obtained was poured in ice water and acidified with HCl (37%). The white precipitate was filtered and dried, yielding 149g (94.4%) white product. m.p. 174°C. IR (KBr) 3015 (νOH), 1692 (νC=O), 742, 720 cm^{-1}(νCH aromatic). NMR ($(CD_3)_2CO$,σ, ppm): 2.87 (t, CH_2CO), 4.53 (t, NCH_2), 6.9-7.5 (m, 6 aromatic protons), 7.92 (d, 2 aromatic protons).

N-(2-hydroxyethyl)-2-(N-carbazolyl)propionylamide.
30g (0.125 mole) of 2-(N-carbazolyl)propionic acid and 200 ml monoethanolamine (large excess) were heated at reflux temperature for 6 hours. The excess monoethanolamine was distilled off under vacuum. The remained solid was dissolved in $CHCl_3$ and the solution was washed with water. The solid obtained after the evaporation of $CHCl_3$ was recrystallized from 1:1 benzene:cyclohexane mixture affording 24.7g (0.0875 mole) (70%) of white crystals. m.p. 111-112°C. IR(KBr): 3280 (νNH), 1630 (amide I), 1535 (amide II), 740, 719 cm^{-1} (νCH aromatic). NMR ($CDCl_3$, σ, ppm): 1.9 (s, OH), 2.68 (t, $COCH_2$), 3.28 (m, NCH_2CH_2O), 4.61 (t, NCH_2), 5.7 (s, NH), 7.0-7.6 (m, 6 aromatic protons), 8.07 (d, 2 aromatic protons).

N-(2-chloroethyl)-2-(N-carbazolyl)propionylamide.
5.7 ml (0.0781 mole) of $SOCl_2$ were added dropwise during 10 minutes under stirring to a mixture of 20g (0.071 mole) of N-2-hydroxyethyl)-2-(N-carbazolyl)propionylamide and 300 ml of CH_2Cl_2 (cooled with ice water mixture). The mixture was stirred one hour at reflux temperature. Then the CH_2Cl_2 was removed on a rotovapor at 30°C and the solid obtained was recrystallized

from a 1:1 benzene:cyclohexane mixture affording 21.44g (95%) of white crystals. m.p. 107-108°C. IR (KBr): 3260 (νNH), 1630 (amide I), 1540 (amide II), 720, 740 cm^{-1} (νCH aromatic). NMR ($CDCl_3$,σ, ppm): 2.50 (t, CH_2CO), 3.15 (s, NCH_2CH_2Cl), 4.5 (t, NCH_2), 5.55 (s, NH), 6.9-7.4 (m, 6 aromatic protons), 8.93 (d, 2 aromatic protons).

2-(2-N-carbazolylethyl)-2-oxazoline.
To a refluxing solution of 0.08 mole of C_2H_5ONa in 75 ml ethanol was added a solution of 20g (0.063 mole) of N-(2-chloroethyl)-2-(N-carbazolyl)propionylamide in 150 ml ethanol. The mixture was stirred under reflux for 20 minutes. Then the NaCl was filtered and the solvent was evaporated on a rotovapor. The solid compound was washed with water, dried and extracted with ethylic ether. Ethylic ether was evaporated at 20°C and the solid product remained was recrystallized from heptane affording 15.9g (95%) white crystals. m.p. 106-107°C. IR (KBr): 1659 (νC=N), 1242 (νC-O), 990, 930, 890 (νCH oxazoline ring), 720, 748 cm^{-1} (νCH aromatic). NMR ($CDCl_3$,σ, ppm): 2.78 (t, CH_2C), 4.55 (t, CH_2N), 3.5-4.3 (m- NCH_2CH_2O), 6.9-7.5 (m, 6 aromatic protons), 7.92 (d, 2 aromatic protons).

3,5-dinitrobenzoyl chloride.
It was obtained from 3,5-dinitrobenzoic acid and $SOCl_2$ (large excess) at reflux temperature. After the excess of $SOCl_2$ was distilled, the obtained solid was used without further purifications.

N-(2-hydroxyethyl)-3,5-dinitrobenzoylamide.
To a stirred solution of 8g (0.13 mole) of monoethanolamine in 350 ml of distilled water was added a solution of 23.06g (0.1 mole) of 3,5-dinitrobenzoylchloride in 100 ml of warm benzene. The emulsion was shaken and cooled with running water during the gradual addition of a 5% solution of 0.13 mole of NaOH. The product precipitated out of the reaction mixture and solidified within a few minutes to an amorphous mass. The mixture was stirred for two hours, after which time the solid amide was filtered and washed with water. The dried product was recrystallized from methanol to afford 23.0g (90%) of white crystals. m.p. 146-147°C. IR (KBr): 3300 (νOH), 3250, (νNH), 1630 (sec. amide I), 1528 (sec. amide II and ν-NO_2), 1340 cm^{-1} (ν-NO_2). NMR($(CD_3)_2CO$,σ, ppm): 3.65 (m, NCH_2CH_2O), 8.6 (s,NH), 9.03 (s, 3 aromatic protons).

N-(2-chloroethyl)-3,5-dinitrobenzoylamide.
A mixture of 20g (0.078 mole) N-(2-hydroxyethyl)3,5-dinitrobenzoylamide and 150 ml of $SOCl_2$ (large excess) was refluxed for two hours. $SOCl_2$ was then evaporated and the solid compound was recrystallized from methanol providing 20.3g (95%) of white crystals. m.p. 144-145°C. IR (KBr): 3274 (νNH), 1625 (sec. amide I), 1520 (sec. amide II and ν-NO_2), 1338 cm^{-1} (ν-NO). NMR ($(CD_3)_2CO$,σ, ppm): 3.65 (m, NCH_2CH_2O), 8.6 (s, NH), 9.03 (s, 3 aromatic protons).

2-(3,5-dinitrophenyl)-2-oxazoline.
To a refluxing solution of 0.083 mole of C_2H_5ONa in 100 ml of

ethanol was added a solution of 19g (0.069 mole) of N-(2-chloroethyl)-3,5-dinitrobenzoylamide in 350 ml of warm ethanol. The mixture was stirred under reflux for one hour. Then the ethanol was removed on a rotovapor and the dark-brown solid was washed with water and dried. Recrystallization from ethanol afforded 10.7g (65%) of light-brown crystals. m.p. 122-123°C. IR (KBr): 1649 (νC=N), 1256 (νC-O), 1528 (ν-NO_2), 1335 (ν-NO_2), 972, 948, 908 (νCH oxazoline ring), 728, 690 cm^{-1} (νCH aromatic). NMR ($CDCl_3$,σ, ppm): 3.9-4.8 (m, CH_2CH_2), 8.98 (s, 3 aromatic protons).

POLYMERIZATIONS

The following experiment was carried out in order to establish the living polymerization mechanism of CEOxz. 0.5726g (2.17 mmole) CEOxz and 0.1188g (0.638 mmole) methyl p-toluensulfonate were degased and then sealed in an ampoule under argon. After 15.5 hours of bulk polymerization at 120°C, NMR analysis of the reaction mixture showed the monomer was completely polymerized and the initiator consumed. According to the NMR assignment from Figure 1, the polymerization degree was calculated to be 3.4. The same value was obtained by GPC measurements and corresponds with the feed ratio monomer:initiator =3.4.

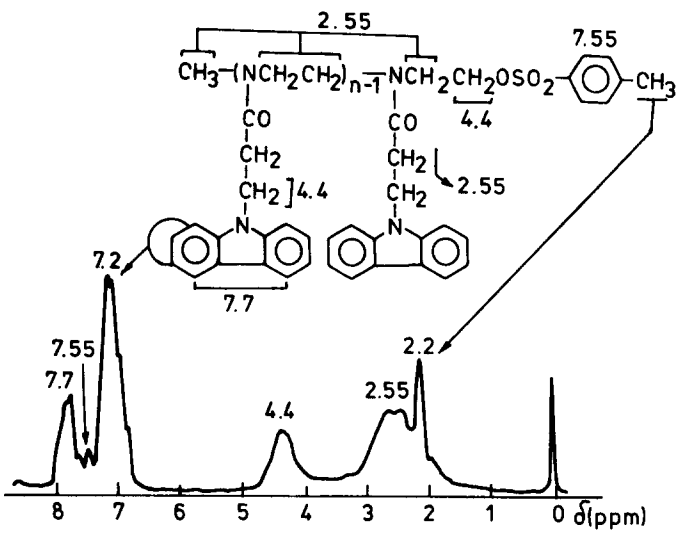


Figure 1

^{1}H-NMR spectrum ($CDCl_3$, 50°C) of poly(CEOxz)

The polymer is soluble in $CHCl_3$, THF and can be purified by precipitation with ethylic ether.

The same experiment was carried out with DNPhOxz, except that the polymerization temperature was 145°C. According to the NMR spectrum from Figure 2, the polymerization degree cor-

responds with the feed ratio between monomer and initiator. The polymer is soluble in DMF, DMSO, THF and can be purified by precipitation with ethylic ether. The similar polymerization experiments carried out in DMF solution take place also through a living mechanism.

DISCUSSION

Attempts to synthesize CEOxz through the thermal isomerization of the corresponding aziridine (Scheme 1) lead to a large amount of poly(CEOxz) because traces of carboxylic acids initiate the polymerization of aziridines. In these conditions, the yield of 2-oxazoline is very low. On the other way, we tried to avoid successive reactions of carbazole derivatives chlorination, because their 3 and 6 positions are very sensitive to chlorination reactions. Working with larger excess of $SOCl_2$ then 1.2:1 (mole of $SOCl_2$ vs mole of carbazole derivatives) usually the chlorination of carbazole ring takes place. From these reasons the synthesis methods presented seem to be the most suitable.

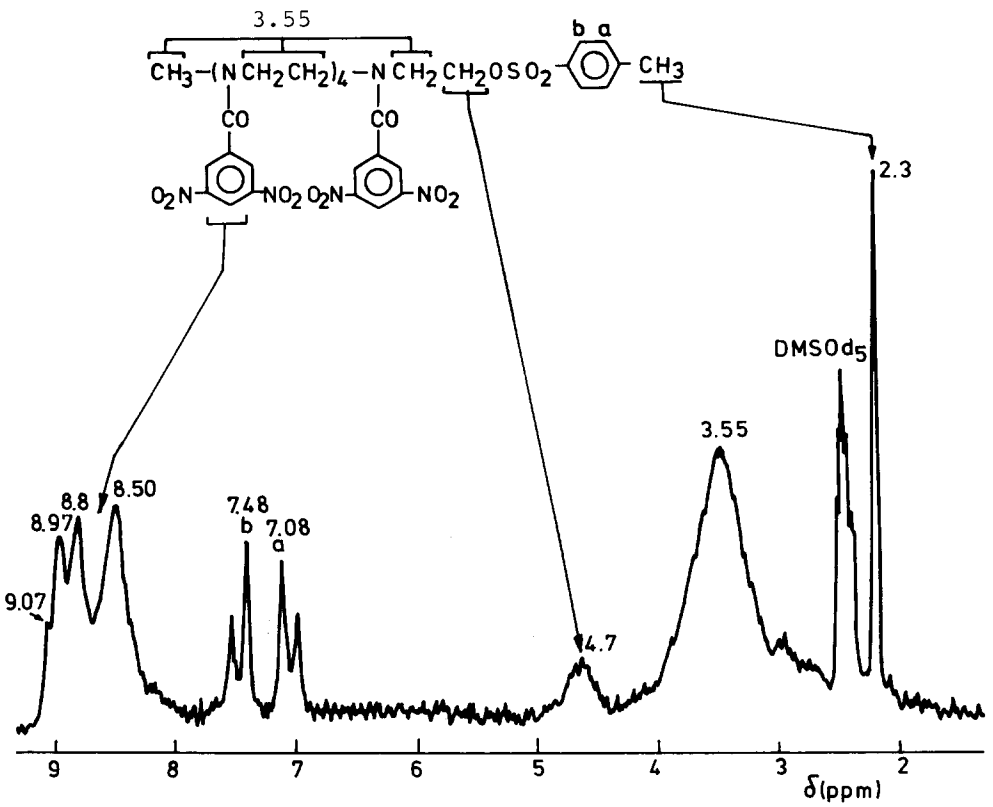


Figure 2

^{1}H-NMR spectrum ($DMSOd_5$, 120°C) of poly(DNPhOxz)

The bulk polymerizations were carried out above the melting point of the monomer. NMR analysis showed no monomer and initiator left in the sample, so conversion to polymer was 100%. Based on the result that the theoretical and experimental polymer molecular weight are the same, a living polymerization mechanism is proposed.

Next paper will present ABA triblock copolymer synthesis containing electron-accepting or electron-donating pendant groups in the A block.

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