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Synthesis and Polymerization of 2-(β-N-Ethylenediphenylamine)-2-Oxazoline

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SUMMARY

The synthesis of 2-(β-N-ethylenediphenylamine)-2-oxazoline and its living cationic polymerization in the presence of methyltosylate are described. This 2-substituted 2-oxazoline was used for the synthesis of a ABA triblock copolymer with poly(N-β-(N-diphenylamine)propionylethylenimine) as A block and poly(ethyleneglycoladipate) as B block.

INTRODUCTION

Polymerization of cyclo imino ethers offered a wide area of research in the last years (SAEGUSA and KOBAYASHI, 1976). Among the studied directions, cationic isomerization polymerization of 2-substituted 2-oxazoline was demonstrated to proceed through the corresponding cyclic onium p-toluensulfonates (oxazolinium) as propagating species when initiated by alkyltosylates, and in several cases via a living polymerization mechanism (SAEGUSA et al., 1972, 1974; SIMIONESCU et al., 1981; PERCEC, 1981a, 1981b).
The present paper describes the synthesis of 2-(β-N-ethylenediphenylamine)-2-oxazoline (EDPAOxz) and its cationic bulk polymerization in the presence of methyltosylate, in order to establish the living polymerization mechanism. Poly(ethyleneglycoladipate) with tosyl end groups (PEGA-Ts) was then used to initiate the cationic polymerization of EDPAOxz in order to obtain a ABA type block copolymer with poly(N-β-(N-diphenylamine)propionyl ethylenimine) as A block (hard part) and poly(ethyleneglycoladipate) as B block (soft part).

EXPERIMENTAL

2-(β-N-ethylenediphenylamine)-2-oxazoline (EDPAOxz) was synthesized according to the scheme:

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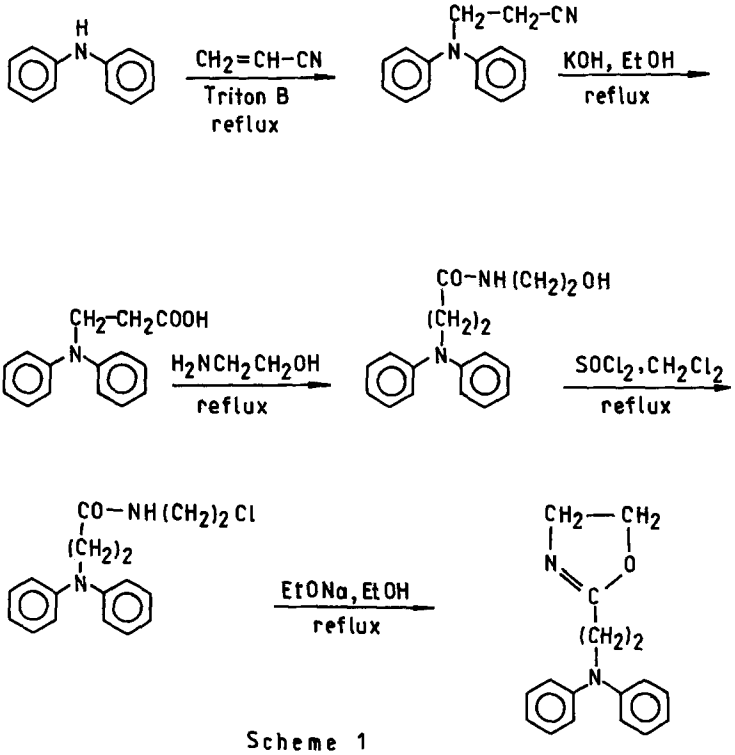

Scheme 1

2-(N-diphenylamine)propionitrile was synthesized by cyanoethylation of diphenylamine (85 g, 0.5 mole) with acrylonitrile (150 ml, 40% in excess) in the presence of 4 ml of benzyltrimethylammonium hydroxide (Triton B). The reaction mixture was stirred at reflux temperature for 4 hours. The unreacted acrylonitrile was then distilled off, and the reaction product was separated from the unreacted diphenylamine by low pressure distillation above 150°C. The yield was 60 g (55%) and the ^{1}H-NMR spectrum of 2-(N-diphenylamine)propionitrile showed signals (ppm) at 2.3 (triplet, CH_2CN), 3.3 (triplet, CH_2N), 6.9 (multiplet aromatic). The spectrum was registered without solvent.

2-(N-diphenylamine)propionic acid was obtained by hydrolysis of 2-(N-diphenylamine)propionitrile. To 56 g (0.25 mole) of 2-(N-diphenylamine)propionitrile, 400 ml ethanol, 20 g KOH and 200 ml water were added. The mixture was stirred at reflux temperature until complete dissolution (ca. 4 hours). The solution was poured in a ice-water mixture, acidified with HCl up to pH 6.5--7.0. A white product precipitated, then it was filtered and dried under vacuum. The yield was 54 g (90%).

The ^{1}H-NMR spectrum ($CDCl_3$, room temperature) showed signals (ppm) at 2.79 (triplet, CH_2CO), 4.18 (triplet, CH_2N), 7.12 (multiplet aromatic) and 8.05 (broad singlet, COOH).

N-(2-hydroxyethyl)-2-(N-diphenylamine)propionylamide. A mixture of 24 g (0.10 mole) of 2-(N-diphenylamine) propionic acid and 100 ml monoethanolamine (large excess) was stirred at reflux temperature about 6 hours. The monoethanolamine excess was then distilled at low pressure; the viscous product was solved in $CHCl_3$, the solution washed several times with water and $CHCl_3$ was evaporated from the organic layer. The solid product was recrystallized from 1:1 cyclohexane:benzene mixture. 17.5 g (62%) of white crystalline product were obtained. The ^{1}H-NMR spectrum ($CDCl_3$, 60°C) showed signals (ppm) at 2.5 (triplet, CH_2CO), 2.7 (singlet, OH), 3.1-3.7 (multiplet, CH_2-CH_2), 4.01 (triplet, CH_2N), 6.0 (broad singlet, NH) and 6.92 (multiplet aromatic).

N-(2-chloroethyl)-2-(N-diphenylamine)propionylamide. To a mixture of 15 g (0.053 mole) N-(2-hydroxyethyl)--2-(N-diphenylamine)propionylamide and 250 ml CH_2Cl_2, 4.7 ml (0.064 mole) $SOCl_2$ were added dropwise, at room temperature. The mixture was stirred one hour at reflux. The CH_2Cl_2 and $SOCl_2$ excess were evaporated on a rotovapor. The solid product was dried under vacuum, yielding 13.5 g (85%). The ^{1}H-NMR spectrum ($CDCl_3$, 60°C) showed signals (ppm) at 2.5 (triplet, CH_2CO), 3.2 (singlet, CH_2-CH_2), 4.5 (triplet, CH_2N), 5.7 (broad singlet, NH) and 6.92 (multiplet aromatic).

2-(β-N-ethylenediphenylamine)-2-oxazoline. To a solution of 0.048 mole of C_2H_5ONa in 45 ml ethanol at reflux temperature, 12 g (0.045 mole) N-(2-chloroethyl)-2-(N-diphenylamine)propionylamide in 100 ml ethanol were added. The mixture was stirred at reflux temperature during 20 minutes. The precipitated NaCl was filtered; ethanol was evaporated in a rotovapor. The remaining liquid was washed with water, dried and extracted with ethylic ether. The ethylic ether was then evaporated and the solid product was recrystallized from heptane to give 8.0 g (75%) of a white crystalline product. The ^{1}H-NMR spectrum of the product is given in Figure 1.

Instrumental analysis. IR spectra were registered on a Perkin-Elmer 577 spectrophotometer (KBr pellets) and the NMR spectra on a C 60-HL JEOL spectrometer, operating at 60 MHz.

Homopolymerization of EDPAOxz. 0.267 g (1 mmole) EDPAOxz and 0.065 g (0.35 mmole) methyl p-toluensulfonate were degased and sealed in an ampoule, under argon. After 24 hours of bulk polymerization, at 120°C, the ^{1}H-NMR spectrum of the reaction mixture showed no more monomer or initiator signals. The

degree of polymerization, calculated from the NMR spectrum (Figure 2), DPn = 2.5, is in fairly good agreement with the initial monomer/initiator ratio (2.8).

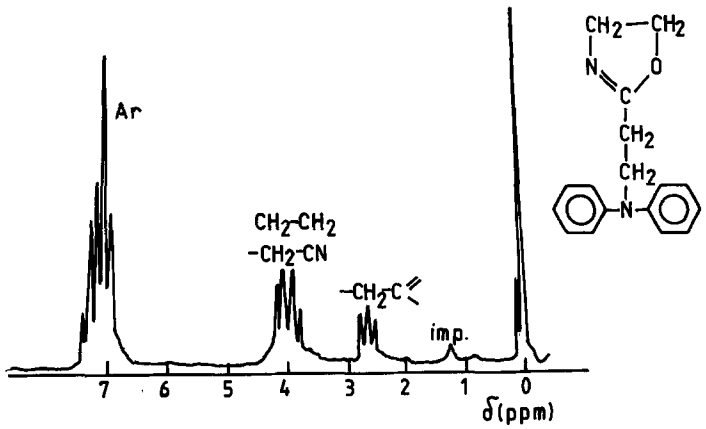

Fig. 1. ^{1}H-NMR spectrum of EDPAOxz

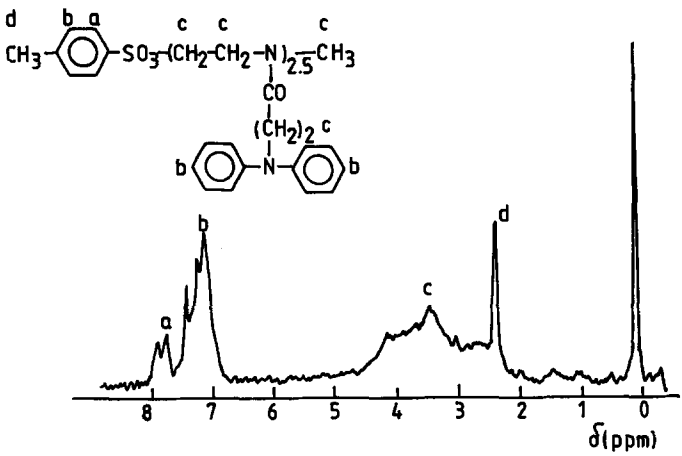

Fig. 2. ^{1}H-NMR spectrum ($CDCl_3$, 20°C) of poly(EDPAOxz)

Synthesis of EDPAOxz-PEGA-EDPAOxz block copolymer. The ABA triblock copolymer with poly(N-β-(N-diphenylamine)propionyl ethylenimine) as A block and poly(ethyleneglycoladipate) as B block was synthetised using PEGA-Ts as initiator. PEGA with OH end groups was esterified with tosyl chloride, to obtain PEGA-Ts, according to PERCEC (1981b).
A mixture of 0.45 g (1.69 mmole) EDPAOxz and 0.50 g (0.19 mmole) PEGA-Ts was degased and sealed in an am-

poule under argon. After 24 hours of bulk polymerization at 120°C, the mixture was dissolved in $CHCl_3$, precipitated in ethylic ether and reprecipitated from the same system. The yield was found to be 95%.

RESULTS AND DISCUSSION

PEGA was a commercial product having -OH end groups ($\bar{M}_n$=1900, functionality 2).
IR and NMR spectra confirmed, for PEGA-Ts, the total tosylation of -OH groups. The IR spectrum of PEGA-Ts showed the disappearance of the 3500 cm^{-1} band (-OH groups) (Figure 3). The 750 and 820 cm^{-1} bands were assigned to the tosyl aromatic groups and the bands at 1170 and 1370 cm^{-1} to the ester sulfonated groups. The NMR spectrum of PEGA-Ts showed also the complete disappearance of $-\underline{CH_2}OH$ protons signal, confirming the quantitative tosylation. The molar mass of PEGA-Ts, determined by NMR, was $\bar{M}_n$=2606 (DPn = 13).

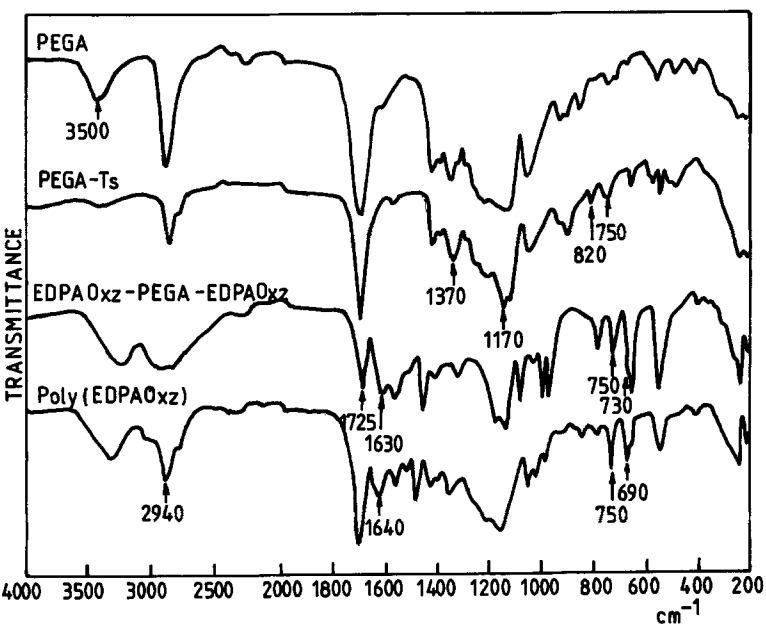

Fig. 3. Typical IR spectra (KBr pellets)

IR and NMR analysis of the block copolymer confirmed the expected structure and composition. The IR spectrum presented a strong band at 1630 cm^{-1}, due to the amide group (Figure 3) and two bands at 730 and 750 cm^{-1}, assigned to the aromatic groups. The ^1H-NMR spectrum of the block copolymer is presented in Figure 4.

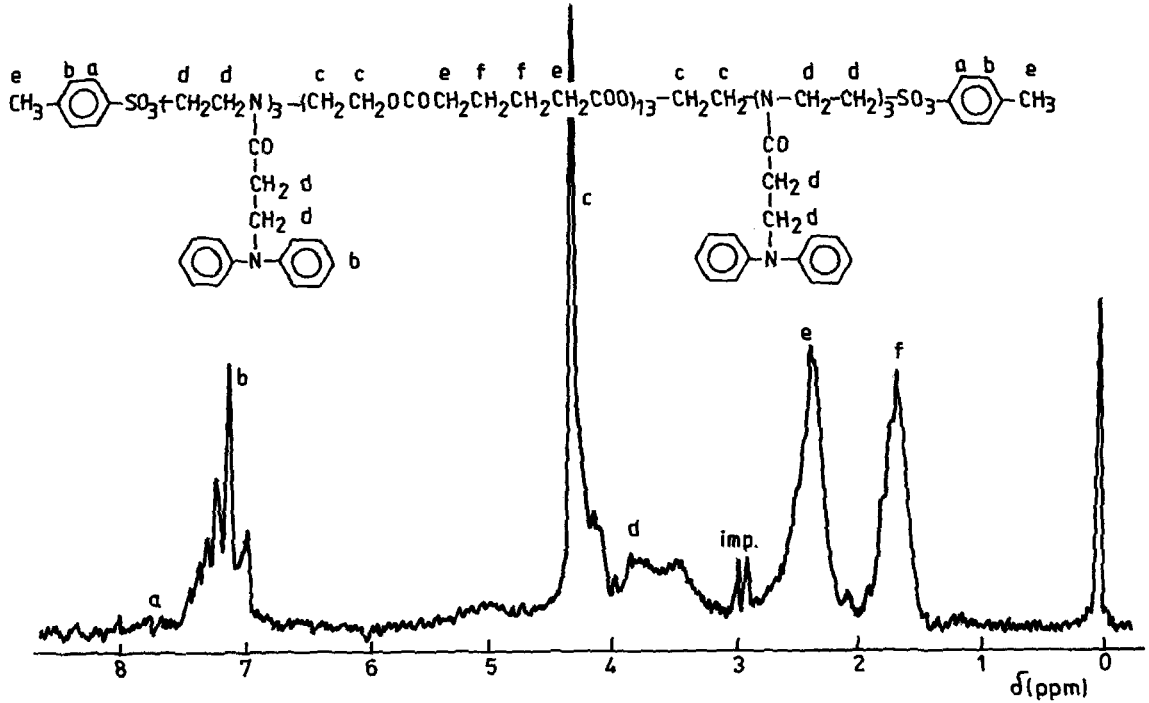

Fig. 4. ^{1}H-NMR spectrum of EDPAOxz-PEGA-EDPAOxz block copolymer ($CDCl_3$, 20°C)

The composition of the block copolymer, calculated according to this spectrum, is in good agreement with the theoretic one (Table 1).

TABLE 1
Composition of EDPAOxz-PEGA-EDPAOxz block copolymer

PEGA-Ts mmole	EDPAOxz mmole	DPn of A block theor.	DPn of A block expt.	Poly EDPAOxz/PEGA (struct. unit. molar ratio)	
				theor.	expt.
0.19	1.69	4.5	3.0	0.69	0.46

CONCLUSIONS

The synthesis of EDPAOxz was presented. Its polymerization through a living mechanism with alkyltosylates as initiator was demonstrated, using methyltosylate for homopolymerization and PEGA-Ts for ABA type triblock copolymer formation; the composition of this triblock copolymer was in good agreement with the calculated one.

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