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Triblock Copolymers of 2-Substituted-2-Oxazoline and Poly(Ethylene Oxide)

Cristofor I. Simionescu and Idir Rabia*

"P. Poni" Institute of Macromolecular Chemistry, Alley Gr.Ghica Vodă No. 41 A,
R-6600 Jassy, Romania

SUMMARY

α,ω-p-toluensulphonic acid ester of poly(ethylene oxide) was synthesized and used to initiate the cationic isomerization polymerization of 2-(β -N-carbazolylethyl)-2-oxazoline and 2-methyl-2-oxazoline.The polymerization was carried out in bulk,and ABA type block copolymers containing poly(N-acetyl ethylenimine) or poly N- (N-carbazolyl)propionylethylenimine blocks (A block) and poly(ethylene oxide) blocks (B block) were obtained.

INTRODUCTION

The polymerization of cyclic imino ethers has been studied by many groups over the last years (1-8).Among the obtained results it was shown that the polymerization of 2-substituted 2-oxazoline initiated by methyltosylate proceeds via a living polymerization mechanism (3). On the other hand the synthesis of ABA type block copolymers was performed by macromolecular initiation of 2-substituted-2-oxazoline polymerization with α,ω-telechelic polymers having p-toluensulphonic acid esters at both chain ends (8-11).

The present paper describes the synthesis of two block copolymers of an ABA type. Poly(ethylene oxide) with -OH end groups was first esterified with tosylchloride and further used to initiate the bulk polymerization of 2-methyl-2-oxazoline (MeOxz) and 2-(β-N-carbazolylethyl)-2-oxazoline (CEOxz). In this way block copolymers containing poly(N-acetylethylenimine) or poly N- (N-carbazolyl)propionylethylenimine as A block (hard part) and poly(ethylene oxide) as B block (soft part) have been synthesized.

EXPERIMENTAL

Reagents: MeOxz was a commercial sample used without further purification.CEOxz was synthesized according to a litterature method (6),(7).Tosyl chloride (commercial product) was recrystallized from petroleum ether. α,ω-poly(ethylene oxide)glycol (PEO) (M_n=2200) was a commercial product which was purified by reprecipitation from its $CHCl_3$ solution with ethylic ether and dried in vacuo at 60°C.

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* Visiting scientist, permanent address: Ecole Nationale Polytechnique d'Alger (Belfort), Algerie

Preparation of p-toluensulphonic acid ester of α,ω-poly(ethylene oxide) glycol (PEO-Ts)

Tosyl chloride (95 g,0.05 mole) was added to a stirred solution of PEO (20 g,0.009 mole,0.018 -OH mole) in a tetrahydrofuran (THF) (150 ml) $-NEt_3$ (7ml ,0.05 mole) mixture.The mixture was kept at 20°C for 4 days under stirring.$Et_3N.HCl$ was separated by filtration ; the product was isolated by precipitation in cold ethylic ether and purified by reprecipitation (three times) from its THF solution with cold ethylic ether. The isolated polymer was dried at 30°C in vacuo to yield 15 g.

Preparation of Oxz-PEO-Oxz block copolymers

A mixture of Oxz and PEO-Ts was degased,and then the ampoule was sealed under argon.After 15 hours polymerization at 120°C, the reaction mixture was cooled and precipitated in ethylic ether,filtred and reprecipitated with ethylic ether from $CHCl_3$ the yield was near 100 % in all cases.

Instrumental analysis

NMR spectra was registered on a C 60-HL JEOL spectrometer operating at 60 MHz. Infrared spectra (IR) were registered on a PERKIN-ELMER 577 spectrphotometer (KBr pellets).

RESULTS AND DISCUSSION

Tosylation of PEO : IR and NMR spectra confirmed for PEO-Ts,the total tosylation of -OH groups. The IR spectrum (Fig.1) of PEO-Ts showed the complete disappearance of the

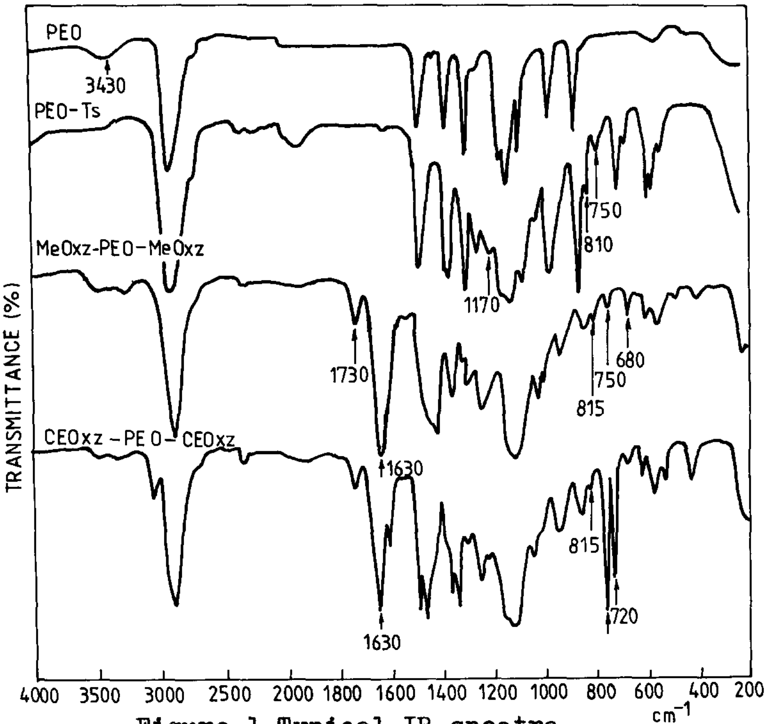

Figure 1-Typical IR spectra

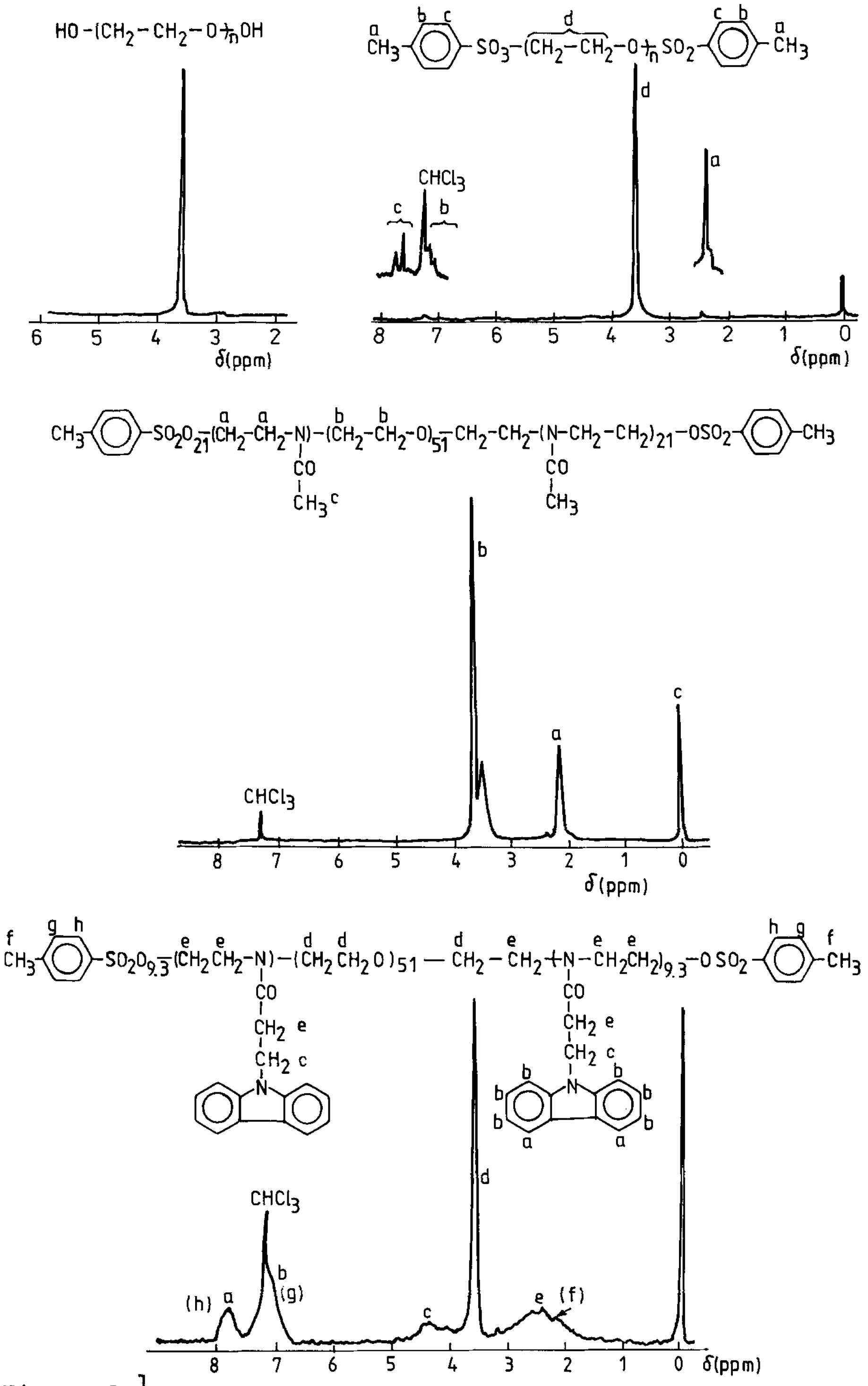

Figure 2: ^{1}H-NMR of PEO,PEO-Ts,block no.3 and block no.5(CDCl$_3$)

band at 3430 cm^{-1} (due to -OH group) and the appearance of absorptions at 750 and 810 cm^{-1} ascribed to the tosyl aromatic groups and at 1170 cm^{-1} assigned to the sulphonate ester group. The ^{1}H-NMR spectrum of PEO-Ts (Fig.2) showed the appearance of two doublet signals at δ=7.65 and δ=7.2 ppm due to aromatic protons and the singlet at =2.4 ppm due to methyl protons of tosyl group. The molecular weight determined from this NMR spectrum is M_n = 2658.

Characterization of block copolymers

The IR spectra of block copolymers (Fig.1) were characterised in addition to the conventional bands of PEO by the strong absorption band at 1630 cm^{-1} assignable to the amide C=O group and the absorptions due to the C-H bending vibrations of the aromatic ring (at 680,750 cm^{-1} and respectively 720, 750 cm^{-1}). Typical ^{1}H-NMR spectra of these copolymers with protons assignement are presented in Fig.2. The block copolymer compositions, calculated according to these spectra, are presented in Table 1, and they are in fairly good agreement with the theoretic values. This means that the living cationic mechanism is also valid for the polymerization of 2-oxazoline 2-substituted initiated by PEO-Ts.

Table 1- Synthesis of ABA block copolymers containing Poly(MeOxz) (No.1-3) and Poly(CEOxz)(No.4-5) as A blocks and PEO as B block.

No.	PEO-Ts mmole	Oxz. mmole	DP_n of A block	DP_n of A block	PolyOxz/PEO (struct. unit.molar ratio)	
			theor.	expt.	theor.	expt.
1.	0.3	9	15	17	0.58	0.65
2.	0.4	8	10	10.8	0.38	0.41
3.	0.4	16	20	21	0.77	0.82
4.	0.2	2	5	5.8	0.19	0.22
5.	0.2	4	10	9.3	0.38	0.37

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