Polymer Bulletin 7, 217-222 (1982)

Polymer Bulletin

Triblock Copolymers of 2-Methyl-2-Oxazoline and Poly(Ethyleneglycoladipate)

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SUMMARY

2-methyl-2-oxazoline was polymerized by using poly(ethyleneglycoladipate) having tosylate end groups as an initiator. Polymerization was carried in bulk,and ABA type block copolymers were obtained containing poly(N-acetylethylenimine) as A block (hard part) and poly(ethyleneglycoladipate) as B block (soft part).

INTRODUCTION

It is well known that the cationic isomerization polymerization of 2-methyl-2-oxazoline initiated by methyltosylate proceeds through the growing species of oxazolinium tosylate via a living mechanism (SAEGUSA et al., 1972). On the other hand, the synthesis of block copolymer containing poly(N-acylethylenimine) was performed with macromolecular initiation of cyclic imino ethers polymerization (SAEGUSA and IKEDA, 1973; SEUNG and YOUNG, 1980; PERCEC,1981; SIMIONESCU et al.,1981, and 1982). In many cases α,ω-telechelic polymers having p-toluen sulphonic acid esters at both chain ends were used as initiators for ABA type block copolymers. This present paper describes the use of poly(ethyleneglycoladipate) with tosyl end groups (PEGA-Ts) to initiate the polymerization in bulk of 2-methyl-2-oxazoline (MeOxz). In this way block copolymers containing poly(N-acetylethylenimine) as A block (hard part) and poly(ethyleneglycoladipate) as B block (soft part) have been synthesized. They are models for ABA thermoplastic elastomers (HOLDEN et al.,1969).

EXPERIMENTAL

Reagents : MeOxz was a commercial sample used without further purification. Tosyl chloride (TsCl) (commercial product) was recrystallized from petroleum ether. α,ω-poly(ethyleneglycoladipate) glycol (PEGA) was a commercial product which was purified by reprecipitation from its $CHCl_3$ solution with ethylic ether and dried in vacuo at 60°C. M_n = 1900.

0170-0839/82/0007/0217/$ 01.20

Preparation of p-toluensulfonic acid ester of α,ω-poly(ethyleneglycoladipate) glycol (PEGA-Ts)

Tosyl chloride (15 g, 0.079 mole) was added to a stirred solution of PEGA (25 g, 0.013 mole ; 0.026 -OH mole) in a tetrahydrofuran (THF) (200 ml)-triethylamine (NEt_3) (11.5 ml, 0.079 mole) mixture. The mixture was kept at 20°C for 4 days with stirring.Then the $Et_3N.HCl$ was separated by filtration.The product was isolated by precipitation in ice water $NaHCO_3$ solution and purified by reprecipitation (three times) from its THF solution with cold ethylic ether.The isolated polymer was dried at 35°C in vacuo.Yield : 16.5 g.

Preparation of MeOxz-PEGA-MeOxz block copolymers

A mixture of MeOxz and PEGA-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 product was a white powder soluble in $CHCl_3$, THF and insoluble in benzene (which dissolved PEGA-Ts) and in water (which dissolved polyOxz).The yield was near 100 % in all cases.

Instrumental analysis

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

RESULTS AND DISCUSSION

Tosylation of PEGA

$$\underset{I}{\mathrm{HO - PEGA - OH}} \quad + \quad \mathrm{TsCl} \longrightarrow \underset{II}{\mathrm{TsO - PEGA - OTs}}$$

The IR spectrum of α,ω-poly(ethyleneglycoladipate) glycol was characterized by the absorption of primary alcohol groups of polymer ends at 3500 cm^{-1} (Fig. 1) . The NMR spectrum showed a triplet at δ=3.85 ppm due to CH_2OH end groups protons.From these results the structure of PEGA is well determined.

In the IR spectrum of PEGA-Ts (Fig.1) the absorptions at 750 and 820 cm^{-1} are ascribed to the benzene ring of tosylate and the absorptions at 1170 and 1370 cm^{-1} are assigned to the sulfonate ester group.The absorption at 3500 cm^{-1} in the starting PEGA disappeared by tosylation.The NMR spectrum of PEGA-Ts (Fig.2) showed the complete disappearence of $-CH_2OH$ protons signal and the appearence of aromatic and $-CH_3$ signals from tosyl groups.These results clearely indicate quantitative tosylation of the OH groups of PEGA.The molar mass of PEGA-Ts determined by NMR , was M_n = 2606 (DP_n = 13).

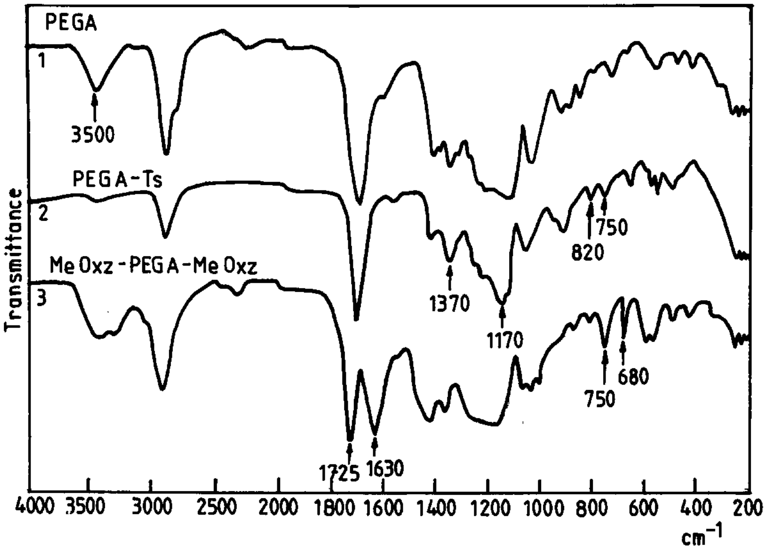


Figure 1: Typical IR spectra

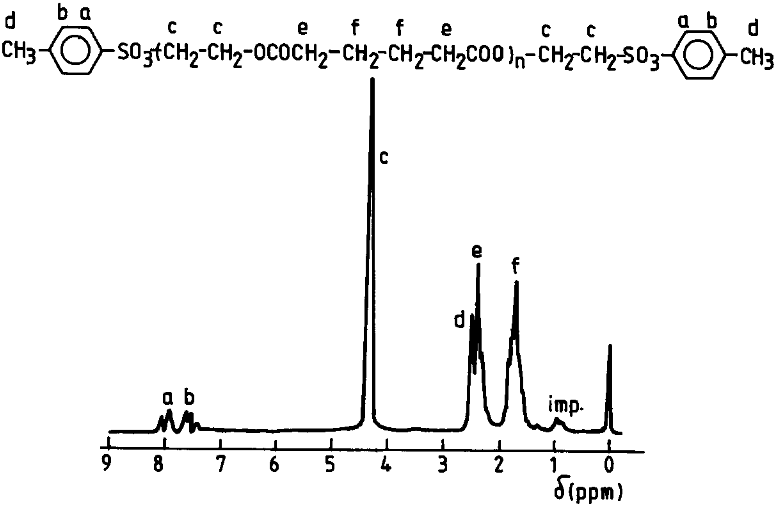
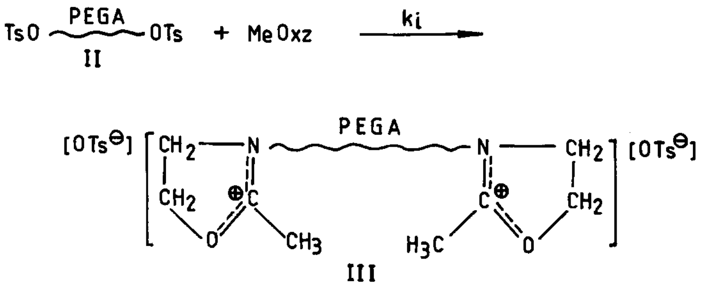


Figure 2: ^{1}H-NMR spectrum of PEGA-Ts ($CDCl_3$, 50°C)

Characterization of block copolymers

The polymerization of MeOxz by PEGA-Ts is considered to proceed according to the reaction scheme which has been proposed for the Oxz polymerization initiated by alkyl tosylates (SAEGUSA et al.,1973).

Initiation



Propagation

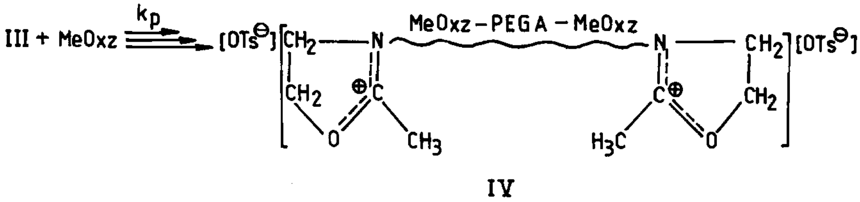


TABLE 1

Synthesis of ABA block copolymers containing Poly(MeOxz) as A block and PEGA as B block.

No.	PEGA-Ts mmole	MeOxz mmole	DP_n of A block		Poly(MeOxz)/PEGA (struct.unit.molar ratio)	
			theor.	expt.	theor.	expt.
1	0.54	17.80	16.5	19.5	2.53	3.00
2	0.29	1.78	3.0	3.4	0.47	0.52
3	0.22	1.78	4.0	4.2	0.61	0.64
4	0.26	7.12	14.0	16.6	2.15	2.55
5	0.27	2.95	5.5	6.0	0.85	0.92

The IR spectra of block copolymers (Fig.1) showed absorptions of the conventional bands of PEGA and a strong band at 1630 cm^{-1} assignable to the amide groups CO. A typical ^{1}H-NMR spectrum of one of these copolymers with protons assignement is presented in Fig.3.

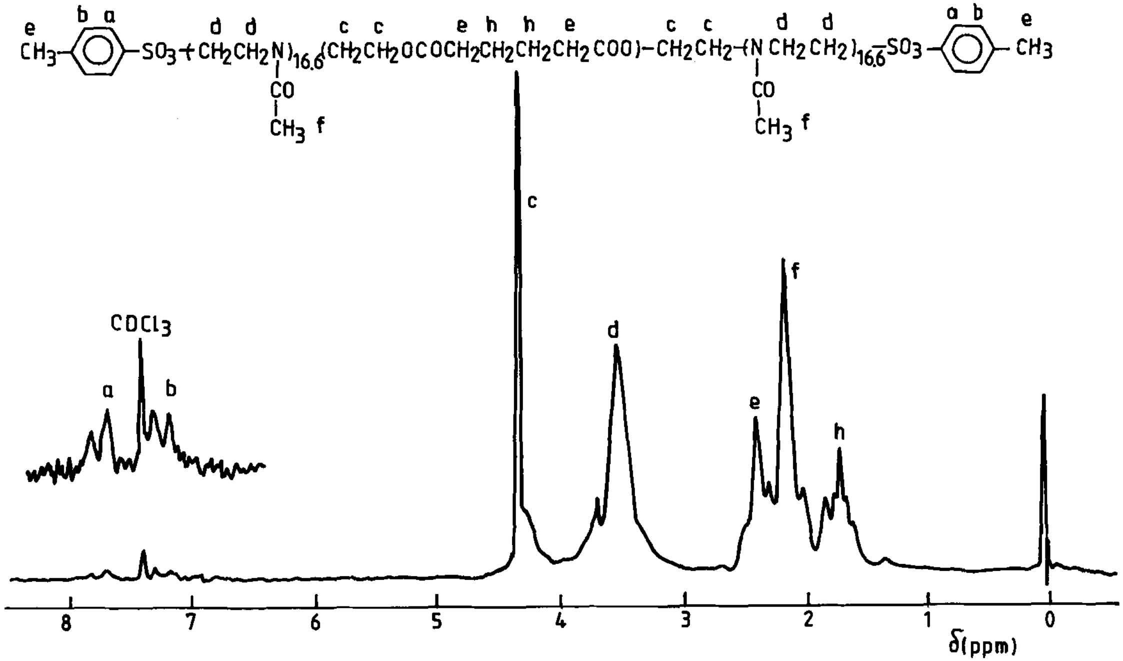


Figure 3: ^{1}H-NMR spectrum of MeOxz-PEGA-MeOxz block ($CDCl_3$,50°C)

The block copolymer compositions determined from the NMR spectra are presented in Table 1 and they are in fairly good agreement with the theoretic calculations. This means,that the living cationic mechanism is also valid for polymerization of MeOxz initiated by PEGA-Ts.

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Received April 6, accepted April 7, 1982