Polymer Bulletin 5, 643–649 (1981)

Polymer Bulletin

Synthesis of ABA Triblock Copolymers Containing Electrono-Donor or Electrono-Acceptor Pendant Groups in A Blocks

Virgil Percec

Institute of Polymer Science, University of Akron, Akron, OH 44325, USA

SUMMARY

α,ω-p-Toluensulphonic acid ester of poly(ethyleneglycoladipate) was synthesized and used to initiate the cationic isomerization polymerization of 2-phenyl-2-oxazoline, 2-(β-N-Carbazolylethyl)-2-oxazoline and 2-(3,5-dinitrophenyl)-2-oxazoline. ABA triblock copolymers containing poly(N-benzoylethylenimine), poly[N-β(N-carbazolyl)propionyl ethyleneimine] or poly(3,5-dinitrobenzoylethylenimine) blocks (A block) and poly(ethyleneglycoladipate) blocks (B block) have been synthesized.

INTRODUCTION

In some previous papers it was shown that both intra- and interchain charge transfer interactions[1,2] give rise to thermally reversible networks. The aim of this paper is to present the synthesis of ABA type block copolymers containing electrono-donor or electrono-acceptor pendant groups in A block. A previous paper[3] presents the synthesis and living cationic isomerization polymerization of 2-(β-N-carbazolylethyl)-2-oxazoline(CEOxz) and 2-(3,5-dinitrophenyl)-2-oxazoline(DNPOxz). The living character of cationic polymerization of these two monomers was proved both in DMF solution and in bulk. The initiator used in these experiments was methyltosylate.

The literature data provide already two ways for the synthesis of cyclic imine ether containing block copolymers. The addition of a second monomer to the nonterminating polymerization of the first one[4], or the initiation of the cyclic imino ether polymerization by a macromolecular initiator[5-9]. ABA type block copolymers were synthesized by using α,ω-telechelic polymers having p-toluensulphonic acid esters[5] or haloalkyl groups[6-9] at both chain ends as initiators.

In the block copolymer synthesis from this paper, poly(ethyleneglycoladipate) (PEGA) with -OH end groups was first esterified with tosylchloride and, then, poly(ethyleneglycoladipate) with tosyl end groups was used to initiate the polymerization of 2-phenyl-2-oxazoline (POxz), 2-(β-N-carbazolyethyl)-2-oxazoline (CEOxz) and 2-(3,5-dinitrophenyl)-2-oxazoline (DNPOxz). In this way, ABA block copolymers containing poly(N-benzoylethylenimine), poly(N-β-(N-carbazolyl)propionylethylenimine) or poly(N-3,5-dinitrobenzoylethylenimine) blocks (A block) and poly(ethyleneglycoladipate) blocks (B block) have been synthesized. The block copolymers of the present

0170-0839/81/0005/0643/$ 01.40

study are characterized by the combination of a soft part of poly(ethyleneglycoladipate) and a hard part containing electrono-donating or electrono-accepting pendant groups. This is the first example of block copolymer containing electrono-accepting groups in one of its blocks.

EXPERIMENTAL

2-Phenyl-2-oxazoline was synthesized and purified according to a literature method^{10}. It was distilled twice under reduced pressure onto sodium. 2-(β-N-Carbazolylethyl)-2-oxazoline and 2-(3,5-dinitrophenyl)-2-oxazoline were synthesized as in the previous paper^{3}. Dimethylformamide (DMF) was dried over molecular sieves (4Å) and distilled under argon before use. Tosylchloride (commercial product) was recrystallized from petroleum ether. Poly(ethyleneglycoladipate) was a commercial product with -OH end groups and $\overline{M}n$ = 1900. It was used without further purification.

Preparation of p-Toluensulfonic Acid Ester of α,ω-Poly(ethyleneglycoladipate)glycol (PEGA-Ts)

Tosyl chloride (12.0g, 0.063 mole) was added to a stirred solution of PEGA (20g, 0.01 mole; 0.02 -OH mole) in a tetrahydrofuran (THF) (150 ml) -NEt$_3$ (9 ml, 0.063 mole) mixture. The mixture was kept at 20°C for 4 days with stirring. Then the Et$_3$N.HCl was separated by filtration. The product was isolated by precipitation in ice water NaHCO$_3$ solution and purified by the precipitation (three times) from its THF solution with cold petroleum ether. The isolated polymer was dried at room temperature in vacuo. Yield: 11.0g.

Preparation of Oxz-PEGA-Oxz Block Copolymers

A mixture of Oxz and PEGA-Ts was degassed, the desired amount of DMF was added and then the ampoule was sealed under argon. After 12.5-13.0 hrs. polymerization at 120°C the reaction mixture was cooled and precipitated in ethylic ether, filtered and reprecipitated with ethylic ether from chloroform (POxz and CEOxz block copolymers) or THF (DNPOxz block copolymers) solutions. The yield was near 100% in all cases.

RESULT AND DISCUSSION

Poly(ethyleneglycoladipate) was a commercial product with -OH end groups ($\overline{M}n$ = 1900) having -OH funtionality f = 2.0. Its IR spectrum presents the absorption of primary alcohol groups of polymer ends at 3500 cm^{-1} (Fig. 1).

The ^{1}H-NMR spectrum of PEGA-Ts (Fig. 2) showed at δ = 3.81 ppm the signal of methylene protons from -CH$_2$-OH groups. The molecular mass determined from the NMR spectrum is $\overline{M}n$ = 1900.

The IR spectrum of PEGA-Ts (Fig. 1) does not present the band at 3500 cm^{-1} (due to -OH group). The absorption at 760 and 820 cm^{-1} are ascribed to the benzene ring of tosyl group and the absorptions at 1170 and 1370 cm^{-1} are assigned to the sulphonate ester group. These data indicate almost quantitative tosylation of -OH groups of the parent polymer. The ^{1}H-NMR spectrum of PEGA-Ts confirms the complete disappearance of -$\underline{CH}_2$OH protons which indicates a quantitative tosylation of -OH groups. The protons of the tosylated -$\underline{CH}_2$-OH groups appear together with those of -O(CH_2)$_2$O- at δ = 4.23 ppm. Two doublets at δ = 7.71 and δ = 7.3 ppm are due to aromatic protons and the singlet at δ - 2.61 is due to methyl protons of tosyl group. Considering that the functionality is again f = 2.0, the molecular mass determined from this NMR spectrum is $\overline{M}n$ = 2493. The obtained block copolymers are soluble in $CHCl_3$, DMF, THF (POxz and CEOxz block copolymers) or DMF, THF (DNPOxz block copolymers) but not in CCl_4 or C_6H_6 (solvents for PEGA but not for corresponding polyoxazolines). The copolymerization yield was near 100% in all cases. Attempts to extract unreacted PEGA with CCl_4 or C_6H_6 failed. This means, the living cationic mechanism is also valid for polymerization of substituted 2-oxazolines with PEGA-Ts.

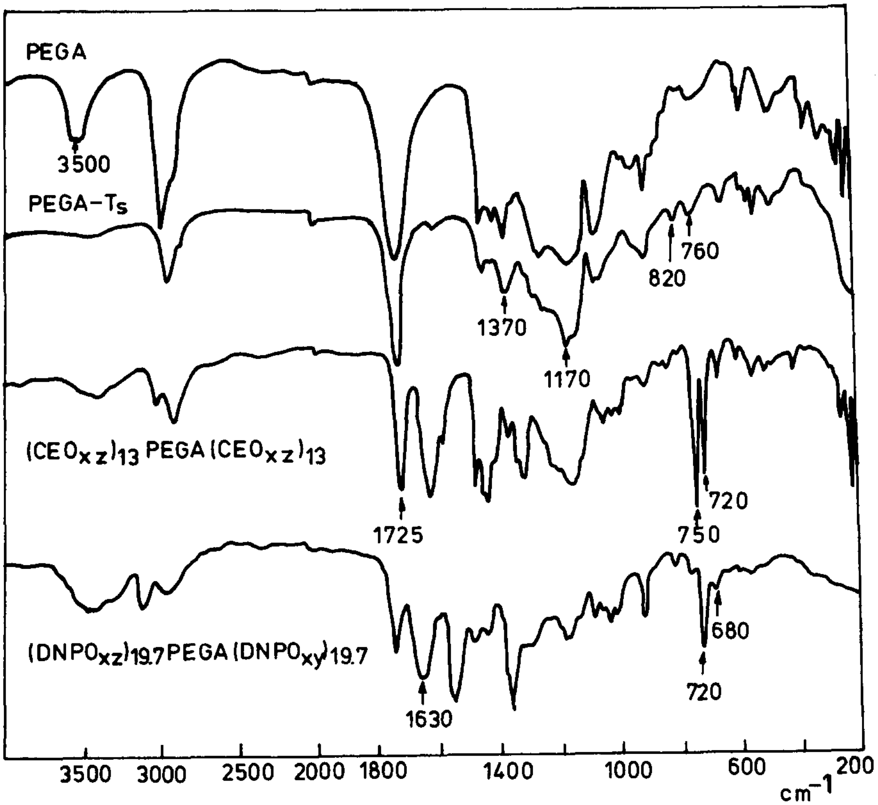

Figure 1: Typical IR spectra (KBr pellets) of: PEGA-Ts, and two triblock copolymers.

The IR spectra of two typical block copolymers are presented in Fig. 1. In addition to the conventional bands of PEGA, a strong band at 1630 cm^{-1} assignable to the amide ν C=O group and the ν CH out of plane from aromatic groups (at 720, 750 cm^{-1} and respective 680, 720 cm^{-1}) appear. Typical ^{1}H-NMR spectra of these copolymers, together with protons assignment are presented in Fig. 2 and Fig. 3. Specially in the case of DNPOxz block copolymers, the tosyl end groups can be detected

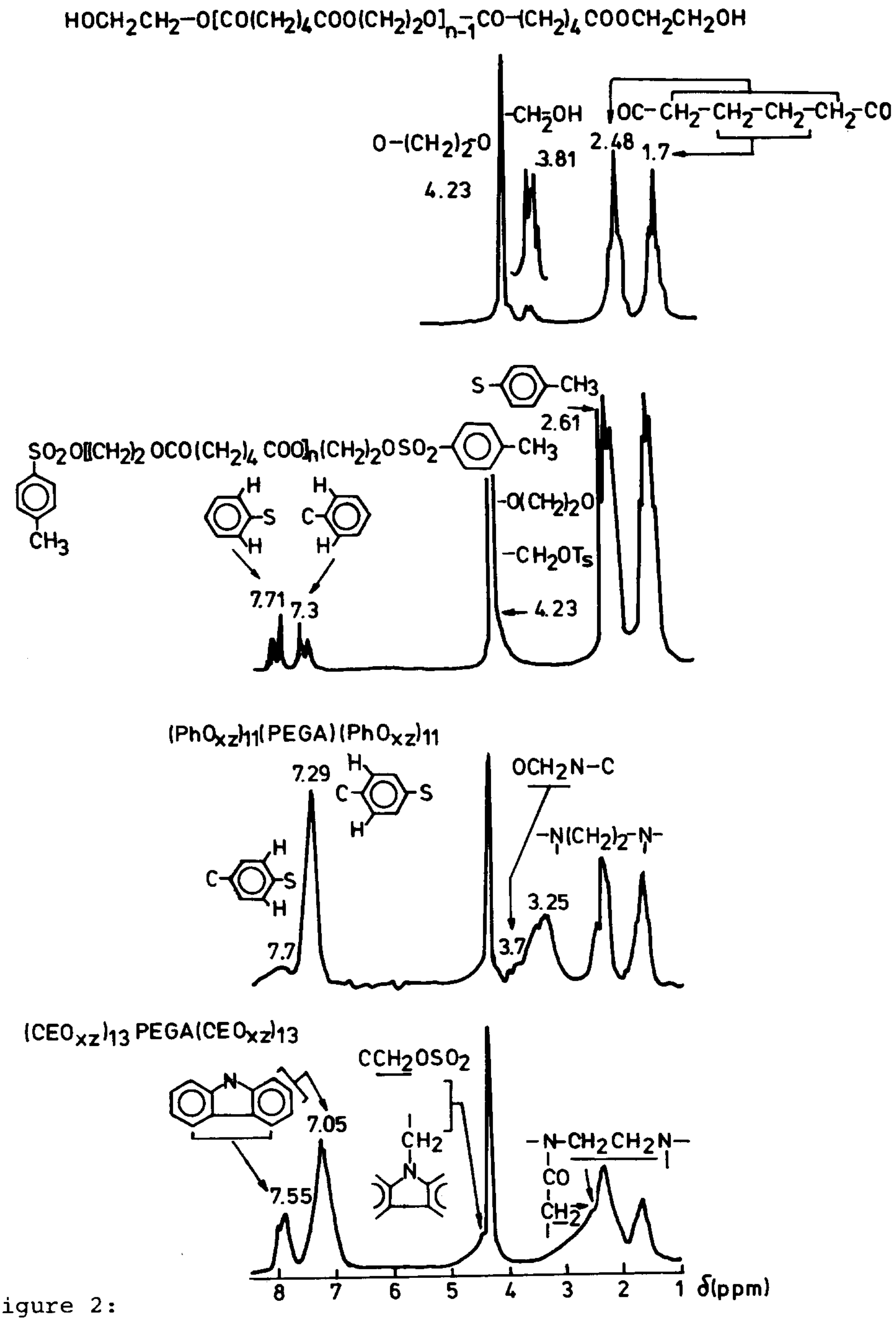

Figure 2:

^{1}H-NMR spectra of PEGA, PEGA-Ts, block no.1 and block no. 5 (CDCl$_3$, 60°C) (TMS)

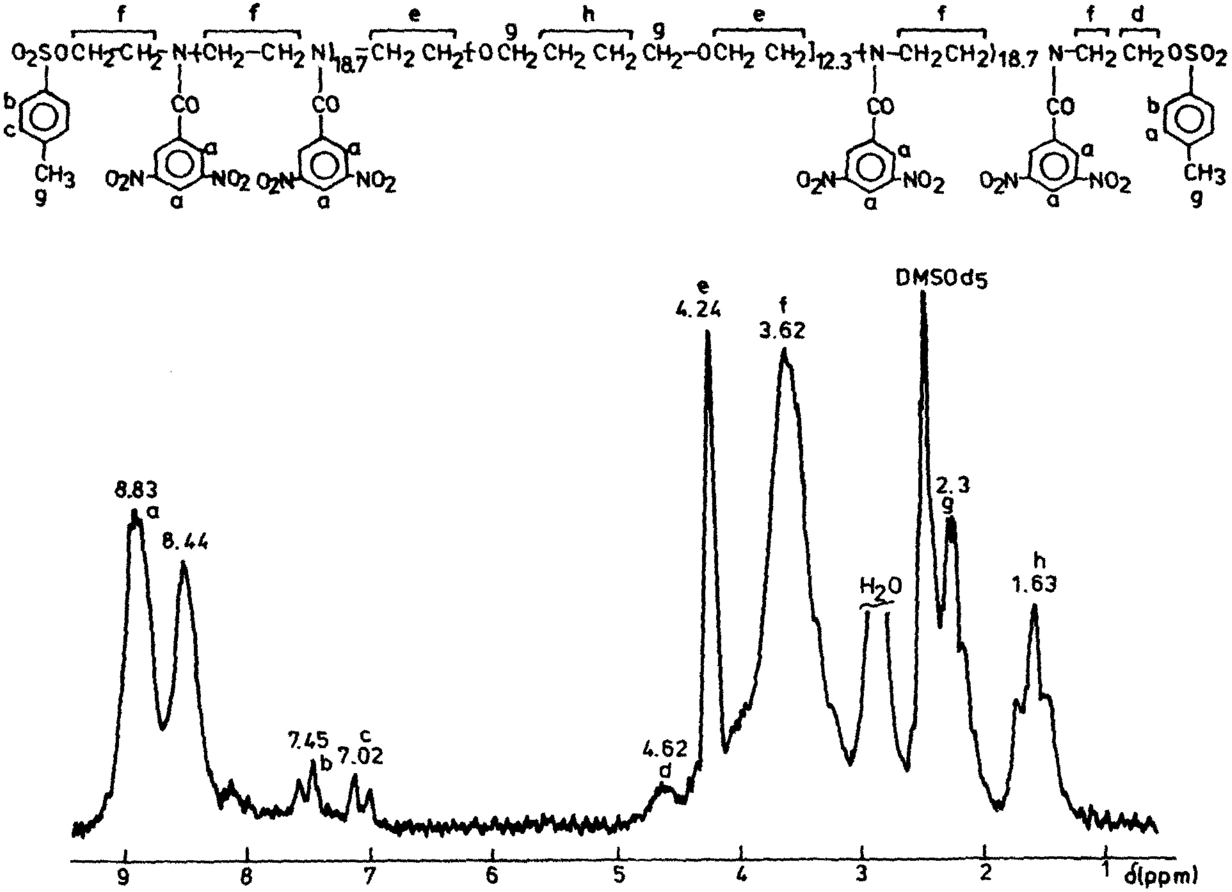

Figure 3: ^{1}H-NMR spectrum of block 7 (DMSOd$_6$, 120°C).

and calculated. The splitting of the aromatic signal of 3,5-dinitrobenzoyl group from the block copolymers can be due to different polymer configurations. The block copolymers compositions determined from the NMR spectra are presented in Table 1 and correspond in the experimental errors limts with the theoretical values.

TABLE 1

Synthesis of ABA block copolymers containing poly(POxz) (No. 1-4) poly(CEOxz) (No. 5-6) and poly(DNPOxz) (No. 7) A blocks and PEGA B blocks. Experimental conditions: solvent/monomer (v/g) = 2.5/1, polym. temp. 120°C; time 12.5-13 hrs.

No.	PEGA-Ts mmole	2-Oxz mmole	DPn of A block	PolyOxz/PEGA(struct. unit molar ratio) theoretic	found(NMR)
1	0.41	9.3	11	1.6	1.4
2	0.22	7.9	18	2.5	2.9
3	0.20	11.2	28	3.9	4.5
4	0.21	20.5	49	6.8	7.1
5	0.24	6.2	13	1.8	2.2
6	0.08	4.7	29	3.9	4.2
7	0.33	8.2	12	1.7	1.6

The GPC curve of a block copolymer shows a unimodal (Fig. 4) molecular weight distribution like in the case of the PEGA, PEGA-Ts or poly(CEOxz), which strongly supports that the obtained block copolymers are free of homopolymers.

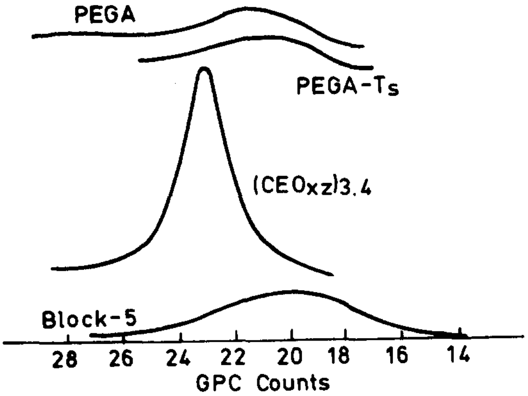

Figure 4: GPC curves (from THF) of PEGA, PEGA-Ts, Poly(CEOxz) and block 5.

In conclusion, pure triblock copolymers containing electrono-donor or electrono-acceptor groups in A block can be obtained through the initiation of the substituted -2-oxazolines polymerization by p-toluensulfonic acid esters of α,ω-hydroxyterminated polymers.

REFERENCES

1. V. Percec, A. Natansohn and C. I. Simionescu, Polym. Bull., 5, 225 (1981)
2. H. J. Cantow, H. A. Schneider and V. Percec to be published
3. V. Percec, Polym. Bull. 5, 651 (1981)
4. M. Litt and J. Herz, Polym. Prepr., 10(2), 905 (1969)
5. T. Saegusa and H. Ikeda, Macromolecules, 6, 805 (1973)
6. S. L. N. Seung and R. N. Young, Polym. Bull., 1, 481 (1979)
7. S. L. N. Seung and R. N. Young, J. Polym. Sci., Polym. Lett. Ed., 17, 233 (1979)
8. S. L. N. Seung and R. N. Young, J. Polym. Sci., Polym. Lett. Ed., 18, 89 (1980)
9. Y. Morishima, T. Tanaka and S. Nozakura, Polym. Bull., 5, 19 (1981)

Received October 4, accepted October 6, 1981