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Living carbocationic polymerization of p-halostyrenes

II. Synthesis of poly(p-chlorostyrene)-*b*-polytetrahydrofuran*

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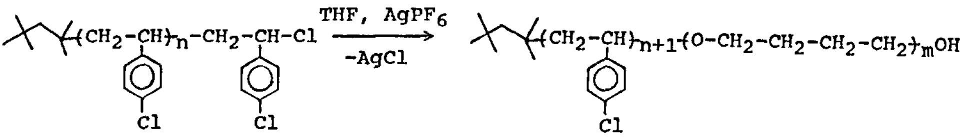
ABSTRACT

The total synthesis of diblock copolymers comprising poly(p-chlorostyrene) (PpClSt) and polytetrahydrofuran (PTHF) segments have been accomplished. The syntheses involved the living polymerization of p-chlorostyrene (pClSt) by the 2-chloro-2,4,4-trimethylpentane/$TiCl_4$ initiating system followed by the blocking of tetrahydrofuran (THF) from the sec-benzylic chlorine end-group of PpClSt in the presence of $AgPF_6$ in THF at room temperature and quenching with methanol:



A series of PpClSt-b-PTHF diblocks have been prepared. The molecular weight of the PTHF segments increased with reaction time. The blocking efficiency (B_{eff}) calculated by ^1H NMR spectroscopy was nearly 100%.

1. INTRODUCTION

Block copolymers are of great interest for both academic and industrial researchers[1]. Recently, living carbocationic techniques have been developed for the preparation of well-defined novel block copolymers[2-4]. In view of the recent developments in the living carbocationic polymerization of pClSt[5] it appeared of interest to investigate the possibility of synthesizing PpClSt-b-PTHf diblock copolymers.

Earlier research in these laboratories has shown that the end structure of PpClSt's obtained by the inifer technique are sec-benzylic chlorines ($-CH_2CH(Cl)pC_6H_4Cl$) and that these end groups initiate the block polymerization of THF in the

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*Paper XXXV in the series of "Living carbocationic polymerization" presence of $AgPF_6$[6]. The present investigations prove that the living carbocationic polymerization of pClSt also yields these sec-benzylic termini because PpClSt's prepared by this technique readily induced the polymerization of THF upon the addition of $AgPF_6$. Further, this paper concerns an adaptation of this diagnostic technique for the synthesis of a series of PpClSt-b-PTHF diblocks.

2. EXPERIMENTAL

2.1 Materials

Details of the total synthesis, purification and characterization of the PpClSt macroinitiator (whose structure is shown in the Abstract) by the $TiCl_4$/pClSt/CH_3Cl:methylcyclohexane (40/60 v/v)/dimethylacetamide/2,6-di-tert-butylpyridine/-80°C system have been described[5]. $AgPF_6$ (Aldrich Chemicals) was used as received. THF was freshly distilled from CaH_2 under a dry nitrogen atmosphere. Methanol, ethanol and methylene chloride (Fisher Scientific Co.) were used as received without further purification.

2.2 Procedure

Blocking experiments were carried out at room temperature inside a dry box under a nitrogen atmosphere. The handling of glassware and chemicals have been described[5,7,8]. A series of large test tubes were charged with 10 mL of THF and a calculated amount (∿0.10 g) of PpClSt macroinitiator ($\overline{M}_n$ = 7,800; $\overline{M}_w/\overline{M}_n$ = 1.80). $AgPF_6$ (0.05 g) dissolved in 10 mL of THF was added to the charge and the reaction was allowed to proceed for 1-5 hours with constant stirring at room temperature. The rapid formation of a white milky precipitate (AgCl) indicated the onset of blocking. Polymerization was stopped by the addition of few mL of methanol. The product was filtered to remove the AgCl and the solvents (including unreacted THF) were evaporated. The product was dissolved in CH_2Cl_2 (good solvent for both PpClSt and PTHF segments) and precipitated into ethanol (good solvent for PTHF, nonsolvent for PpClSt). The polymers were vacuum dried at room temperature overnight and the yields were determined. ^1H NMR analyses were carried out with polymer solutions in $CDCl_3$ (15% w/v).

2.3 Characterization

^1H NMR spectra were recorded by a Varian Gemini 200 MHz instrument. Molecular weights and molecular weight distributions were obtained by a Waters high pressure GPC assembly (Model 6000 A Pump, Microstyragel columns of 10^5, 10^4, 10^3, 10^2, 500 and 100 Å, UV and RI detectors). Elution counts were calibrated by well-fractionated polystyrene standards. THF solutions were used and the flow rate was 1 mL/minute[5,8].

3. RESULTS AND DISCUSSION

Table I summarizes the experimental details and results of five experiments. The PpClSt/PTHF ratio indicates the relative magnitudes of the four aromatic and aliphatic ($-C\underline{H}_2-O-C\underline{H}_2-$) proton resonances, respectively, and has been obtained by integrating the ^1H NMR spectra of diblock copolymers. The $\overline{M}_n$s of the block copolymers were calculated from ^{1}H NMR spectra by the use of these integrated values. According to this calculation the $\overline{M}_n$ of the PpClSt macroinitiator significantly increased upon blocking. The $\overline{M}_n$ of the PTHF segments of the diblocks increased with reaction time. The B_{eff} (mole PpClSt-b-PTHF/mole PpClSt) was close to 100% in all experiments. Previous investigations on the blocking of THF from sec-benzylic end-groups of telechelic PpClSts (prepared by the inifer technique) resulted in close to 90% blocking efficiency[6].

TABLE I

Synthesis and Characterization of PpClSt-b-PTHF

	Time (hour)	PpClSt (g)	Diblock (g)	PpClSt/PTHF	B_{eff} (%)	$\overline{M}_n$* (block)	$\overline{M}_w/\overline{M}_n$
a	1	0.1047	0.1096	33/4	99	8290	1.88
b	2	0.1062	0.1290	58/12	109	8640	1.90
c	3	0.1052	0.1165	65/13	100	8610	1.94
d	4	0.1066	0.1135	48/16	91	9120	1.89
e	5	0.1073	0.1282	36/12	101	9220	1.92

* calculated from proton NMR spectroscopy

Blocking is proposed to start by the abstraction of the terminal sec-benzylic chlorine in PpClSt by $AgPF_6$ (as evidenced by AgCl precipitation) followed by initiation of THF polymerization. According to Burgess et al.[9] the living polymerization of THF can be initiated by organohalides (alkyl, allyl and benzyl) in the presence of $AgPF_6$. Franta et al.[10] polymerized isobutylene and styrene by benzylic halides in the presence of $AgSbF_6$. According to an earlier report[11] 100% B_{eff} could not be obtained with tert-chlorine ended polyisobutylene macroinitiator in conjunction with $AgPF_6$ because tert-chlorine ended polyisobutylenes undergo dehydrochlorination in the presence of this silver salt.

Figure 1 shows the GPC traces of a representative diblock copolymer (sample e) and that of the starting PpClSt macroinitiator (dotted line). The unimodal GPC trace of the PpClSt shifts toward higher molecular weights which indicates significant blocking. Figure 2 shows the proton NMR spectrum with assignments of a representative block copolymer (sample d). The resonance peak at 3.4 ppm indicates the incorporation of PTHF segments in the polymer. Our products are probably pure diblocks: The PTHF was removed by selective dissolution by ethanol (see Experimental) and the symmetric GPC traces (absence of skewing or shoulder toward low molecular weights) indicate the absence of significant amounts of PpClSt. The GPC traces of the series from a to e of diblocks exhibited a gradual shift toward lower elution counts which suggests continuous growth of the PTHF segments. These results are in good agreement with those reported by Zsuga and Kennedy[6].

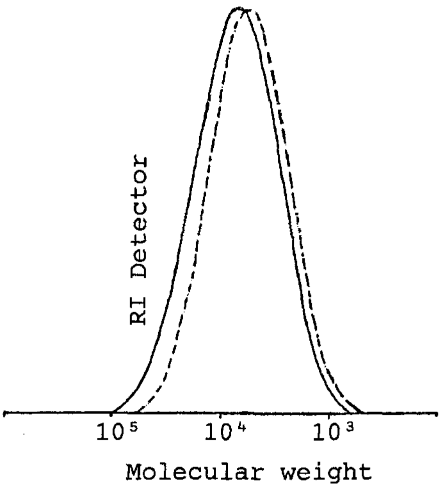

Figure 1. GPC traces of the PpClSt macroinitiator (---) and the PpClSt-b-PTHF block polymer (——)

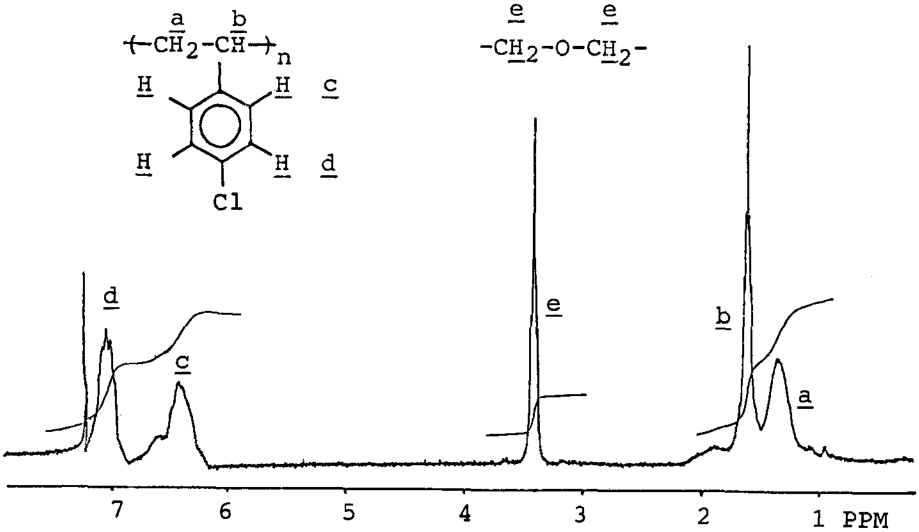

Figure 2. ^1H NMR spectrum of PpClSt-b-PTHF obtained in $CDCl_3$

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