

Synthesis of block copolymer by combination of living cationic and iniferter polymerization systems

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Abstract

Functional polytetrahydrofurans containing N,N' -diethyl dithiocarbamates were synthesized by the living cationic polymerization of tetrahydrofuran using trifluorosulfonic acid anhydride and N,N' -diethyl dithiocarbamic acid sodium salt as an initiator and terminator, respectively. The molecular weight distribution was narrow and the number average molecular weights of the polymer were very close to the theoretical one, $M_{n,th}$. N,N' -diethyl dithiocarbamoyl polytetrahydrofuran was used as a macroiniferter in the photopolymerization of methyl methacrylate and block copolymers were obtained. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Living cationic and radical polymerization; Iniferter; Block copolymer

1. Introduction

The synthesis of block copolymers usually requires efficient controlled/“living” polymerization mechanism. Polymers with a variety of terminal functionalities obtained by “living” cationic polymerization may be useful for initiating another polymerization to yield block copolymers. The examples on the preparation of block copolymers by combination of living cationic and radical polymerization [1–11], living cationic and living radical polymerization have been reported [12–20].

End group functionalized polymer can be synthesized by using a suitable terminator [21,22]. Polytetrahydrofuran can be polymerized without chain transfer and termination reactions under closely controlled conditions [23–25]. The oxonium group of the living chain end can react with nucleophiles and thus gives rise to a variety of functional groups [26–28].

Polytetrahydrofurans containing terminal N,N' -diethyl dithiocarbamate moieties (C-PTHF) were synthesized by the living cationic polymerization of tetrahydrofuran (THF) using trifluoromethanesulfonic acid anhydride (TFA) as an initiator and terminated by N,N' -diethyl dithiocarbamic acid sodium salt. The obtained polymer (C-PTHF) was used as macroiniferter (initiator–transfer agent–terminator)

[12,29–32] in the photopolymerization of methyl methacrylate (MMA) to produce a block copolymer.

2. Experimental

2.1. Materials

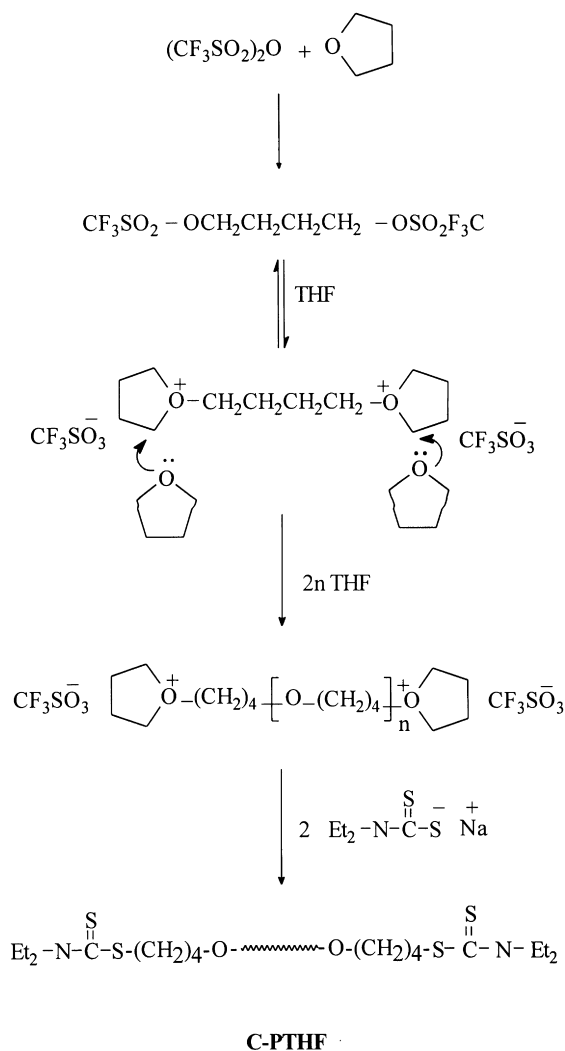
THF was dried over potassium hydroxide, distilled over sodium wire and finally distilled over sodium/benzophenone ketyl prior to use. MMA (Aldrich) was passed through a column containing basic alumina (Type Brockmann 1) and distilled over CaH_2 in vacuo under nitrogen. N,N' -diethyl dithiocarbamic acid sodium salt trihydrate (Fluka) heated to remove water at 180°C at 2 h in vacuo. Triflic anhydride (Aldrich) was used as received. Dichloromethane (E. Merck) was treated with concentrated H_2SO_4 , and washed with Na_2CO_3 solution (5%) and water. After drying with CaCl_2 it was refluxed and distilled over P_2O_5 . Finally, it was stored over activated molecular sieve (type 4 Å).

2.2. Synthesis of N,N' -diethyl dithiocarbamoyl polytetrahydrofuran

N,N' -diethyl dithiocarbamoyl polytetrahydrofuran (C-PTHF) was prepared according to a procedure described previously [11]. A three-necked flask equipped with nitrogen inlet and a rubber septum was connected to a vacuum line. The flask was dried at 130°C under vacuum. After cooling at room temperature, THF (50 ml, 12.3 mol l⁻¹) was distilled into

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Scheme 1.

the flask. The flask was then disconnected under nitrogen and placed into a thermostatically controlled bath. Adding triflic anhydride (0.104 ml , $1.23 \times 10^{-2} \text{ mol l}^{-1}$) induced the initiation of the polymerization under stirring at 25°C . After a given time, an aliquot sample was removed for GPC characterization by a syringe and polymerization was

Table 1

Preparation and characterization of carbamate terminated PTHF ($[\text{THF}] = 12.3 \text{ mol l}^{-1}$ (bulk), $[\text{TFA}] = 1.23 \times 10^{-2} \text{ mol l}^{-1}$, conversion = 14% in 25 min at 25°C)

Run	$M_{n(\text{UV})}^a$	$M_{n(\text{Th})}^b$	$M_{n(\text{GPC})}^c$	$M_{n(\text{GPC-PTHF})}^{c,d}$	M_w/M_n^c
PTHF ^e	—	10 300	16 400	9100	1.13
C-PTHF ^f	10 300	10 600	16 600	9200	1.25

^a Calculated by UV measurement in cyclohexane.

^b Calculated by $M_{n,\text{th}} = ([M]_0/[In]_0) \times MW_0 \times \text{Conversion}$.

^c Obtained by GPC based on calibration with polystyrene standards.

^d Calculated by $M_{n(\text{GPC-PTHF})} = 0.556 \times M_{n(\text{GPC})}$ for PTHF[33].

^e PTHF terminated by basic methanol.

^f $[\text{DC}] = 0.123 \text{ mol l}^{-1}$ in THF.

terminated by the addition of methanol. The remaining part of living PTHF was terminated by the addition of a solution of a N,N' -diethyl dithiocarbamic acid sodium salt (DC) (0.123 mol l^{-1}) in 10 ml of THF. The polymerization mixture was stirred for 15 min at 25°C , poured into methanol and cooled to -30°C . Finally, the precipitated polymer was filtrated off and dried in vacuo.

2.3. Block copolymerization of MMA using C-PTHF

The polymer C-PTHF (0.2 g) was put into a Pyrex tube (i.d. 10 mm) and CH_2Cl_2 (2 ml) and MMA (2 ml) were added. The tube was degassed under high vacuum and sealed under nitrogen prior to irradiation at $\sim 300 \text{ nm}$ in a Rayonet reactor equipped with rotating sample holder. Appropriate cut-off filters were placed in front of the tube.

2.4. Fractionation of block copolymers

After photolysis of the reaction mixtures, block copolymers were separated by precipitation in methanol at room temperature. By cooling the supernatant solution to -30°C and maintaining it at that temperature overnight a second polymer fraction precipitated. Both fractions were dried and characterized by GPC and spectral analysis.

2.5. Analysis of the polymers

IR spectra were recorded on JASCO 500 spectrophotometer using KBr disc. The $^1\text{H-NMR}$ spectra were recorded on a Bruker (model 200) in CHCl_3 solution using tetramethylsilane as the internal standard. UV-Vis spectra were recorded on a Perkin-Elmer (model Lambda 2) spectrophotometer in CH_2Cl_2 solution. GPC analyses were performed with a set-up consisting of a Waters pump (model 600E) and Ultrastayragel columns with porosities 500 and 10^4 \AA , respectively. THF was used as an eluent at a flow rate of 1 ml min^{-1} and were carried out with Waters Differential Refractometer (model 410). Samples were injected by using $20 \mu\text{l}$ sample loop. Concentrations were normally in the range of 2–3% (w/v). Molecular weights were calculated with the aid of polystyrene standards. Molecular weights were multiplied by a factor of 0.556 [33] for PTHF.

3. Results and discussion

α,β -functional polytetrahydrofurans were synthesized by living cationic polymerization of THF using trifluoro-sulfonic acid anhydride as a bifunctional initiator [24,25] at 25°C (Scheme 1). In the case of living polymerization, the theoretical molecular weight of the obtained polymer ($M_{n,\text{th}}$) can be calculated by Eq. (1).

$$M_{n,\text{th}} = ([M]_0/[In]_0) \times MW_0 \times \text{Conversion} \quad (1)$$

where $[M]_0$ and $[In]_0$ are the amount of the monomer and initiator concentrations, respectively. MW_0 is molecular

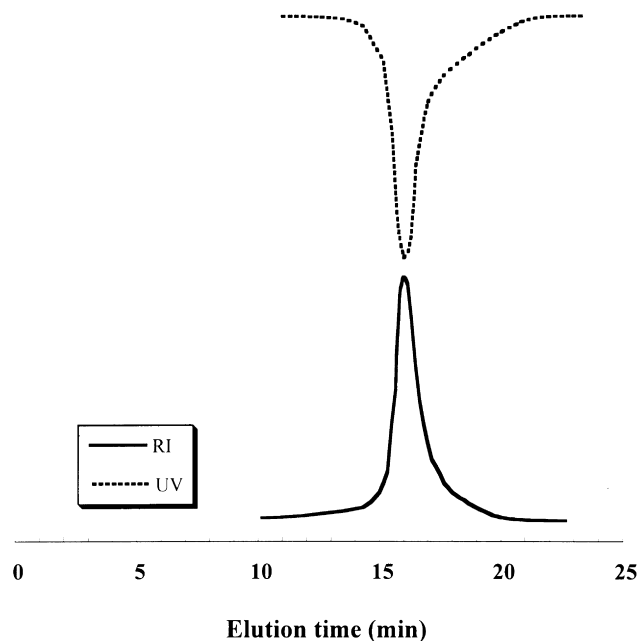


Fig. 1. GPC traces of macroiniferter (C-PTHF) measured by using RI and UV detectors. Standard polymer: polystyrene, eluent: THF, 1 ml min^{-1} .

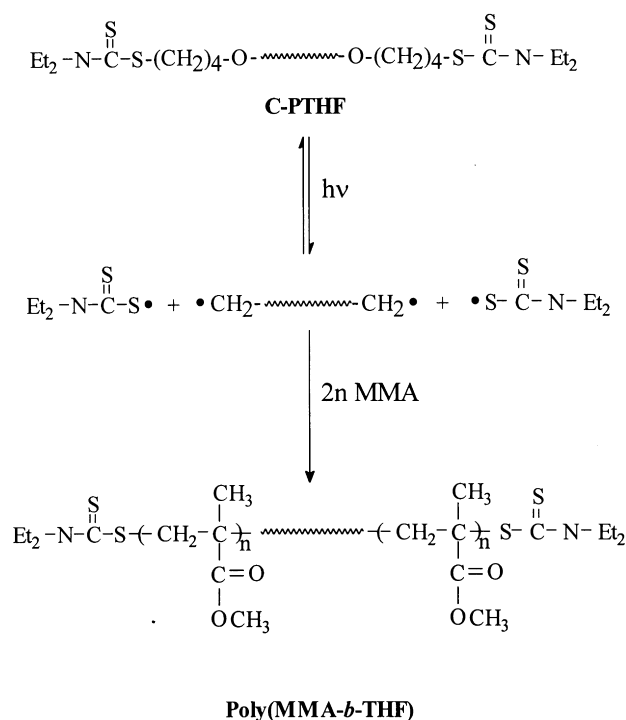
weight of THF (72.11 g mol^{-1}). Comparison of $M_{n,\text{th}}$ to the experimental molecular weights found by UV and GPC analyses indicates approximately two N,N' -diethyl dithiocarbamate units per chain. The results are summarized in Table 1.

As can be seen from Table 1, the number average molecular weights of the obtained polymer determined by GPC ($M_{n(\text{GPC-PTHF})}$) was very close to the theoretical one ($M_{n,\text{th}}$) and the molecular weight distribution was narrow ($M_w/M_n = 1.25$). The peaks measured by GPC with dual RI and UV detectors appeared in the same elution times that indicate that N,N' -diethyl dithiocarbamate group was introduced into the PTHF chain (Fig. 1).

The UV spectra of the polymer show absorption band characteristics of those of the corresponding carbamate groups. Using the value of the extinction coefficient of the methyl diethyl dithiocarbamate ($\epsilon = 13500 \text{ l mol}^{-1} \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 278 \text{ nm}$ in cyclohexane) [29], the molecular weight of C-PTHF was calculated. $^1\text{H-NMR}$ spectrum of the C-PTHF showed a typical PTHF signal for the $-\text{O}-\text{CH}_2-$ protons at 3.4 ppm and for the $-\text{O}-\text{CH}_2-\text{CH}_2-$ protons at 1.6 ppm. The good agreement of the molecular weight values obtained by different methods shows that two functional groups were introduced per chain and polymerization occurred by living cationic mechanism.

C-PTHF was used as a macroiniferter [12,29,32] in the photopolymerization of MMA, and block copolymers were obtained (Scheme 2).

This process leads to the formation of block copolymers. The precursor C-PTHF dissolves in methanol at room temperature and precipitates at low temperature, i.e. $< -20^\circ\text{C}$. The temperature-dependent solubility behavior



Scheme 2.

of low molecular weight PTHF makes it possible to fractionate resulting block copolymers with different MMA segment lengths. This is a natural fractionation and separation of homopolyTHF from the mixture. The separation of the homopolyMMA is not separately performed since there exists no solvent, which is a solvent for homopolyMMA and a non-solvent for homopolyTHF. However, the extraction of homopolyTHF, the indication of a single peak in the GPC curve and the characteristic $^1\text{H-NMR}$ peaks of both segments are a clear evidence for the block copolymer formation.

During the course of polymerization it was observed that conversion and molecular weight of the polymers was increased with irradiation time. The living nature of the system was confirmed by the linear relationship of molecular weight change with conversion (Fig. 2). $^1\text{H NMR}$ spectrum of the block copolymer (Run 2 in Table 2) of MMA by initiation with C-PTHF is shown in Fig. 3. On the basis of a comparison of the ratio of $-\text{OCH}_3$ protons of the MMA group at 3.6 ppm to $-\text{O}-\text{CH}_2-$ protons of the PTHF at 3.4 ppm, the molecular weight of the copolymer ($M_{n(\text{NMR})}$) was calculated. Fig. 4 shows the GPC traces of the block copolymer and macroiniferter. Both the peaks show unimodal molecular weight distribution. The composition of the block copolymers was also analyzed by IR measurements. The IR spectra of the block copolymers display the characteristic carbonyl band at 1730 cm^{-1} and the ether band at 1100 cm^{-1} indicating the existence of both THF and MMA segments. C-PTHF acts as a bifunctional initiator, the obtained block copolymers are expected to be

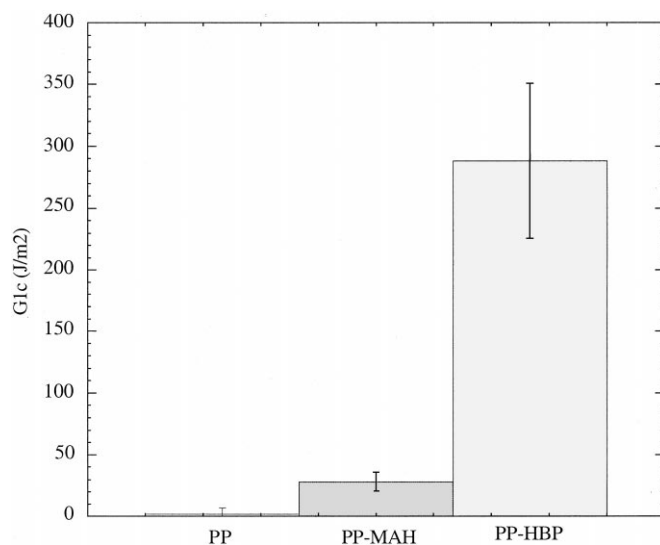


Fig. 2. Conversion versus molecular weight for MMA photopolymerization (room temperature fractions) by C-PTHF at $\lambda = \sim 300$ nm, $\Delta M_n = M_{n_i} - M_{n_o}$, C-PTHF = 0.2 g, MMA = 2 ml, $\text{CH}_2\text{Cl}_2 = 2$ ml, 25°C.

Table 2

Photopolymerization MMA by using C-PTHF as a macroiniferter at $\lambda = \sim 300$ nm. C-PTHF = 0.2 g (3×10^{-3} mol l⁻¹), MMA = 2 ml (4.68 mol l⁻¹), $\text{CH}_2\text{Cl}_2 = 2$ ml, 25°C. Conversion and number average molecular weight data represent values for room temperature fractions

Run	Time (h)	Conversion (%)	M_n^a	M_n^b	M_w/M_n^a	ΔM_n^c
Block-1	1	1.2	80 200	–	1.52	63 600
Block-2	2	8.8	97 400	93 400	1.45	80 800
Block-3	4	11.1	113 700	–	1.49	97 100
Block-4	8	37.1	102 500	–	1.64	85 900
Block-5	16	87.1	157 500	165 000	1.32	140 900

^a Obtained by GPC with RI detector.

^b Calculated by ¹H NMR based on $M_{n(\text{GPC})} = 16\,600$.

^c $\Delta M_n = M_{n_i} - M_{n_o}$.

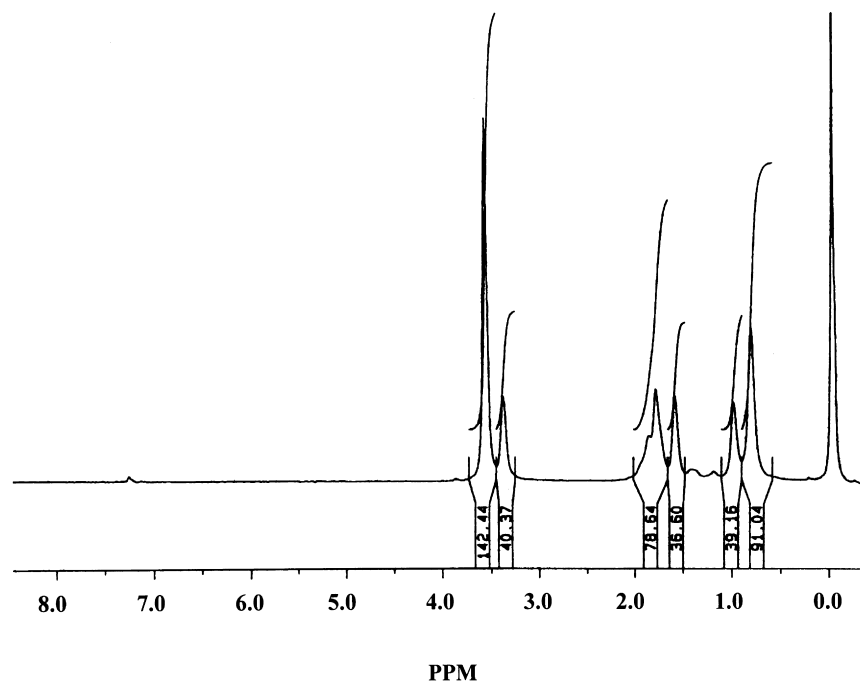


Fig. 3. ¹H-NMR spectrum of block copolymer (room temperature fractions) of MMA and THF in CDCl_3 with TMS.

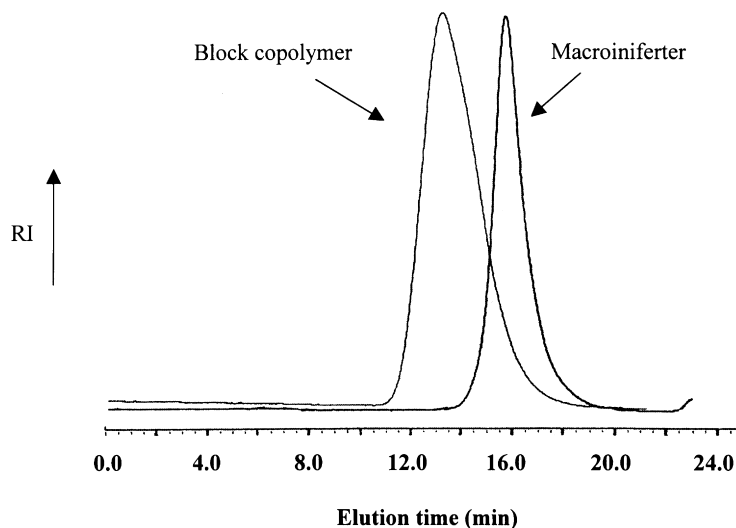


Fig. 4. GPC traces of macroiniferter (C-PTHF) and block copolymer (room temperature fractions) of MMA and THF obtained from C-PTHF. Standard polymer: polystyrene, eluent: THF, 1 ml min^{-1} .

mainly of the ABA type. The overall results of block copolymerization are compiled in Table 2.

In conclusion, polymeric macroiniferters may be prepared by taking advantage of the living polymerization of THF and quantitative quenching of the living end by N,N' -diethyl dithiocarbamates. The photoinitiating capability of the iniferter end groups of this polymer provides a versatile method for preparing block copolymers. In this way, block copolymers of polytetrahydrofuran with MMA were obtained by combination living cationic and living radical polymerization.

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