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FREE-RADICAL SYNTHESIS OF BLOCK COPOLYMERS VIA DIXANTHOGEN-LINKED POLYMER SEQUENCES

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ABSTRACT

Due to high chain transfer and the subsequent terminator properties of the dixanthogen moiety, $(AB)_n$ multiblock copolymers of poly(oxyethylene-*block*-methyl methacrylate) and ABA triblock copolymers of poly(methyl methacrylate-*block*-2-ethylhexyl acrylate) could be synthesized from dixanthogen-linked poly(oxyethylene) and poly(methyl methacrylate) pre-polymer sequences, respectively, using free-radical chemistry. A simple and efficient method was developed for the synthesis of dixanthogen-linked polymers: Hydroxyl-functionalized pre-polymers were reduced using NaH to form alkoxide; CS₂ was then added to the alkoxide to form xanthate; and finally the xanthate was oxidized either in an aqueous or organic medium to form the dixanthogen. The synthesis techniques provided in this paper are general and thus, in principle, can be applied to many other block copolymer systems.

†Deceased April 26, 1993. This article is dedicated to his memory.

INTRODUCTION

The design of block and graft copolymers via free-radical mechanisms is of great commercial interest as an alternative to condensation and ionic polymerization reactions. One such design technique involves exploiting the potential initiator, chain transfer, and terminator properties associated with certain functional groups (e.g., thiuram disulfide) called iniferters [1, 2]. Iniferters are referred to as polyiniferters when the functional group links a multiple sequence of precursor polymer segments and macroiniferters when the functional group forms a bridge between just two precursor polymer segments. The preparation of the final block copolymer can normally be accomplished in a two-step procedure: 1) synthesis of a poly- or macroiniferter, and 2) free-radical polymerization of a second monomer in the presence of the iniferter. The second polymer is invariably capped at both ends with half-fragments of the functional group, hence $(AB)_n$ multiblock and ABA triblock copolymers are formed from poly- and macroiniferters, respectively. Preparation of block, graft, and even star copolymers is possible simply by prescribing an appropriate combination of a functional group and its initial substrate.

Dixanthogen groups ($-\text{OC}(\text{S})\text{S}_2\text{C}(\text{S})\text{O}-$) represent a different class of iniferter. They readily undergo chain transfer and subsequent termination reactions; however, they are not susceptible to thermal scission [3]. Here, one requires either UV light (for photoinitiation) or an independent initiator source in order to begin polymerization [3, 4]. In the present study we adopt the latter method and refer to dixanthogen-linked polymers as ferters.

In this article we report the synthesis of dixanthogen-linked poly(oxyethylene) (POE) and poly(methyl methacrylate) (PMMA) sequences, abbreviated as POEX and PMMAX, respectively. These ferters were derived from α,ω -hydroxy- and α -hydroxy-functionalized polymers. For the POE-based ferters, poly(ethylene glycol) (PEG) and poly(ethylene glycol)methyl ether (PEGME) were utilized, and for the PMMA-based ferters, MMA was polymerized in the presence of 2-mercaptoethanol via the free-radical mechanism. The POEX and PMMAX products were then included in the free-radical polymerization of MMA and 2-ethylhexyl acrylate (EHA), respectively, in order to synthesize the corresponding block copolymers: poly(OE-*block*-MMA) and poly(MMA-*block*-EHA). These particular combinations of polymer blocks are perhaps not novel; however, this is not the immediate concern. The focus of this paper is the simple and efficient route developed for the synthesis of dixanthogen-linked polymers. The practical advantages of forming block copolymers via free-radical mechanisms over traditional and rather more delicate methods are well known. Further, an important corollary of the new POEX molecules is that the dixanthogen group, being inherently hydrophobic yet potentially useful in aqueous systems, is readily soluble in water by virtue of the attached POE segments. Thus, besides block copolymer synthesis, the outcome of this work may also create useful leads in a variety of other applications such as mineral flotation [5] and molecular weight control in aqueous-based polymerizations [6].

EXPERIMENTAL

Chemicals

The ammonium peroxodisulfate (>98.0%), carbon disulfide (>99.9%), chloroform (spectroscopic grade), diethyl ether (>99%), iodine (99.8%), metha-

nol (>99%), 2-mercaptoethanol (98%), PEG (molecular weight, $M = 400, 1500$ and 4000), potassium hydroxide (AR grade), sodium hydride (60% in mineral oil; 99% dry), tetrahydrofuran (THF; >99.5%), and toluene (99%) were obtained from Prolabo (France); the dibenzo-18-crown-6 (98%), PEG ($M = 3400, 8000$), PEGME ($M = 2000$), tetrabutylammonium hydrogen sulfate (97%) were obtained from Aldrich; the MMA and EHA, distilled under reduced pressure, were provided by Rhône-Poulenc; and the 2,2'-azoisobutyronitrile (AIBN) was supplied by SFOS (France). The water was distilled and deionized.

Synthesis of Dixanthogen-Linked Polymers

The hydroxyl-functionalized polymers for the POEX syntheses were commercial PEG and PEGME; and those for the PMMAX syntheses were prepared by bulk polymerizations of MMA initiated by AIBN in the presence of 2-mercaptoethanol. Two such polymerizations were carried out under different conditions (Table 1). The polymer products of these polymerizations were purified by repeated precipitation from an excess of methanol and redissolution in THF, followed by drying at 40°C under reduced pressure.

Table 2 lists the quantities used for each synthesis of POEX and PMMAX. For POEX, the synthesis of alkoxide was performed either by agitating finely ground KOH in a solution of PEG or PEGME in THF at 70°C; or by stirring a mixture of NaH, PEG, and toluene at the dissolution temperature of polymer (in practice, between 25 and 35°C, depending on the value of M). The presence of the mineral oil associated with NaH did not noticeably affect the synthesis of POEX (or PMMAX). The CS₂ was added slowly to the resultant alkoxide at room temperature, and the synthesis of xanthate was complete within half an hour. This reaction is very exothermic, and the temperature must be efficiently controlled in order to avoid the appearance of by-products. The oxidation of xanthate to form dixanthogen was performed either in the oil phase in which the xanthate was prepared or, following extraction of the xanthate, in the aqueous phase. In the oil phase, iodine was used as an oxidizer. A sufficient amount of I₂ was added until its color became persistent. For the aqueous phase oxydation, (NH₄)₂S₂O₈ was used and a ratio of 1.5 mol (NH₄)₂S₂O₈ per mol hydroxyl was found to be adequate. In both cases the temperature has to be maintained below 5°C and the oxidizer has to be added slowly. The POEX products were extracted into water in the case of oil-phase oxidations, and all POEX products were purified by dialysis in water (Spectrum, MWCO 500). The same procedures of syntheses were adopted for PMMAX, using NaH to form the alkoxide and I₂ as the oxidizer. The PMMAX was purified by the same method used to purify the hydroxylated PMMA.

TABLE 1. Recipes Used for the Synthesis of Hydroxylated PMMA

Experiment	MMA, mL	AIBN, g	2-Mercaptoethanol, g	Temp., °C	Final % conversion
PMMA-OH 1	400	2.63	3.12	70	~ 50
PMMA-OH 2	300	0.20	4.70	70	10

TABLE 2. Recipes Used for the Synthesis of Xanthate

	Experiment							
	POEX-						PMMAX-	
	1	2	3	4	5	6	7	8
PEG (g):								
<i>M</i> = 400	—	—	—	—	—	1.00	—	—
<i>M</i> = 1500	—	—	—	—	—	3.75	—	—
<i>M</i> = 3400	—	2.0	10.0	—	—	—	—	—
<i>M</i> = 4000	—	—	—	20.0	—	—	—	—
<i>M</i> = 6000	—	—	—	—	30.0	—	—	—
PEGME (g):								
<i>M</i> = 2000	2.0	—	—	—	—	—	—	—
PMMA-OH (g):								
1. $\langle M \rangle_n = 3010$	—	—	—	—	—	—	20.0	—
2. $\langle M \rangle_n = 5960$	—	—	—	—	—	—	—	15.0
THF (mL)	10	10	50	—	—	—	—	—
Toluene (mL)	—	—	—	40	60	10	40	30
KOH (g)	0.3	0.1	1.5	—	—	—	—	—
NaH ^a (g)	—	—	—	0.60	0.60	0.48	0.50	0.42
CS ₂ (g)	0.25	0.25	1.25	0.80	0.80	0.80	0.61	1.2

^aNaH includes 40% mineral oil.

Syntheses of Block Copolymers

Table 3 summarizes the recipes used for the polymerizations of POEX in bulk MMA and PMMAX in a solution of EHA and toluene. Four polymerizations, using varying concentrations of ferter, were carried out for each of these two systems. For

TABLE 3. Recipes Used for the Polymerization of MMA with POEX and EHA with PMMAX

Experiment	Polymerization medium	[AIBN], mol·dm ⁻³	Temp., °C	[ferter], g·dm ⁻³
POEX3/MMA:				
M1	Bulk MMA	5.0×10^{-3}	80	10
M2				20
M3				52
M4				104
PMMAX1/EHA:				
E1	EHA (2.4 mol·dm ⁻³) in toluene	9.7×10^{-3}	60	4.0
E2				10
E3				20
E4				40

MMA polymerization in the presence of POE-X, AIBN and POE-X were directly dissolved in MMA. The polymerization was carried out in sealed tubes after freezing and degazing the monomer. The reaction was stopped at different times by rapid cooling. The polymer was purified by repeated precipitation from an excess of methanol and redissolution in THF, followed by drying at 40°C under reduced pressure. For EHA polymerization in the presence of PMMA-X, EHA, AIBN, and PMMA-X were dissolved in toluene. The polymerization was carried out in a dilatometer reactor in order to follow the kinetics of the reaction. The block copolymer products were not extracted from the mixture. The initial rates of polymerization were determined by monitoring the fractional conversion as a function of time using gravimetry and dilatometry for MMA and EHA, respectively. For MMA only, the copolymer and any pure PMMA were separated from unreacted POEX at various stages of the reaction up until around 20% conversion by selective precipitation using an excess of diethyl ether, and their average polymer molecular weight was determined.

UV-Visible Spectroscopy

Samples of xanthate and dixanthogen in water or chloroform were analyzed with a UV-visible spectrophotometer (Perkin-Elmer, Lambda 5) using 1 cm × 1 cm quartz cells. Typical spectra of these moieties for aqueous POE-based polymers are presented in Fig. 1.

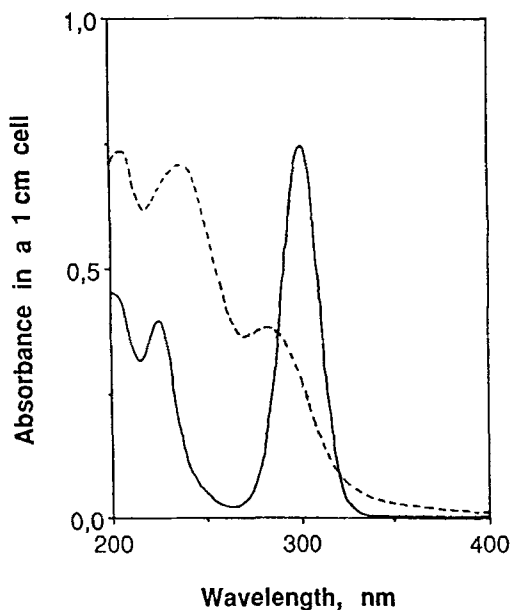


FIG. 1. Typical UV-visible absorption spectra of POE xanthate (—) and POEX (---) in water.

Gel Permeation Chromatography

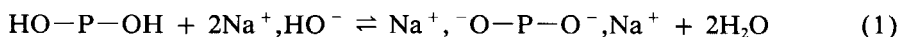
Two separate chromatographs fitted with refractive index detectors (Waters 2000) were calibrated with POE and PMMA standards for measurements using aqueous and organic (THF) eluents, respectively. Molecular weight values were determined using the aqueous eluent for PEG, PEGME, and POEX, and the organic eluent for all other polymers.

RESULTS AND DISCUSSION

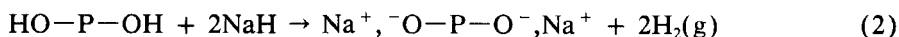
Synthesis of Dixanthogen

The synthesis of dixanthogen from primary alcohols is normally a three-step process: 1) removal of the hydroxyl hydrogens to form alkoxide, 2) addition of CS₂ to the alkoxide to form xanthate (—OC(S)S[−]), and 3) oxidation of the xanthate to form the dixanthogen. The following description outlines the various paths adopted here for this synthesis. Although the example of polymer chosen in these reactions is bifunctional, HO—P—OH, the reaction paths for the monofunctional form are analogous.

Two methods of synthesis were adopted for the first step:

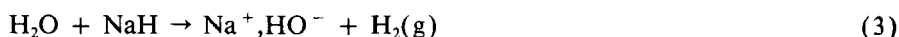


or



The problem with the acid-base reaction (Eq. 1) is finding a suitable solvent which solubilizes both the hydroxide ion and the PEG. Water is a good solvent; however, it is not entirely satisfactory for the acid-base reaction since it will significantly weaken the forward equilibrium represented in Eq. (1) (the pK_a for molecules of the form R—CH₂—OH is around 16 [7]). THF was found to be more suitable; however, heat (70°C) and a large excess of KOH (e.g., 4.5 mol KOH/mol hydroxyl for sample POEX 3, Table 2) were needed. Moreover, the residual water associated with the commercial reagents (especially KOH, which contains 10–15% H₂O) plus the water produced during the reaction (Eq. 1) always limited the yield of alkoxide. Predrying the reagents was not practical for the purpose of this study, and azeotropic distillation (20 mm at 100°C) could not remove all the water. Phase transfer catalysis using either tetrabutylammonium hydrogen sulfate (0.02–0.2 M) or dibenzo-18-crown-6 (0.02 M) did not facilitate the alkoxidation.

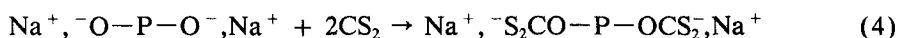
By far the more efficient reaction for alkoxidation is the one which utilized NaH as a reducing agent (Eq. 2). The solvent toluene at just over room temperature was suitable for this reaction. Unlike the reaction with hydroxide, no water is formed and any residual water associated with the commercial products also reacts with NaH to form NaOH:



which can further alkoxidize the hydroxyl groups, as already depicted in Eq. (1). Quantitative UV spectroscopic analysis of the xanthate ($\epsilon = 17,660 \text{ cm}^3 \cdot \text{dm}^{-3} \cdot \text{mol}^{-1}$ for the peak maximum located at 301 nm [8]) indicates that alkoxidation

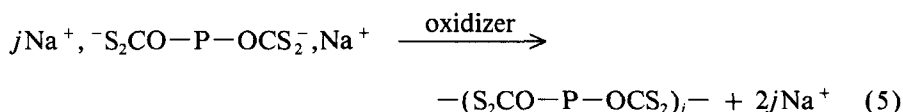
(and hence the CS₂ addition) reaches full expected conversion with relatively small excesses of NaH. For example, only 50 and 20% excesses were required for complete conversion in experiments POEX5 and POEX6, respectively (Table 2). The difference between 50 and 20% excess perhaps reflects the greater water content to hydroxyl ratio of the relatively high molecular weight PEG used in experiment POEX5.

The second step of the dixanthogen synthesis, carried out in toluene:



is relatively straightforward, yielding quantitative amounts of xanthate. After extraction of the xanthate into the aqueous phase, the pH needs to be maintained ≥ 6 to minimize the attack of acid on the xanthate (Fig. 2) [9]. The xanthate will, of course, decompose above pH 6, but this is a relatively slow process.

Oxidation of the xanthates to form dixanthogen was performed using either of two methods: 1) using an oil-soluble oxidizer in the toluene phase, or 2) extraction of the xanthate into the aqueous phase followed by oxidation at $< 4^\circ\text{C}$ using a water-soluble oxidizer. The general reaction scheme for this oxidation is



It is unlikely that all the polymer chains are completely functionalized or that all the xanthates undergo coupling, therefore cyclomers and/or infinitely long chains will not necessarily form as implied in Eq. (5). Note that for the monofunctional polymers only dimers of the original polymer will form: $\text{P}-\text{OC}(\text{S})\text{S}_2\text{C}(\text{S})\text{O}-\text{P}$.

Some characteristics of POEX and PMMAX are summarized in Table 4. Two methods were used to determine the degree of success of oxidation: GPC and UV

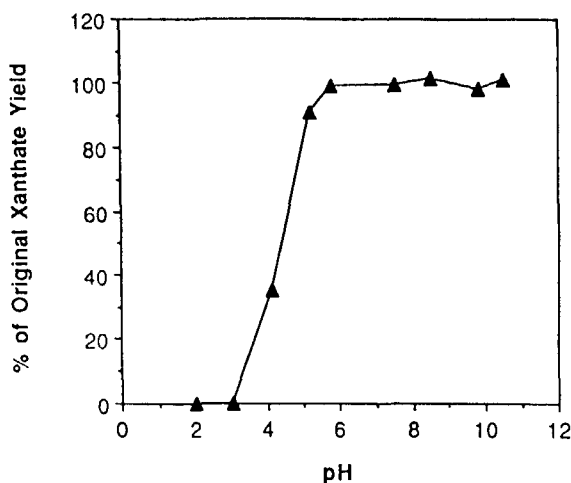


FIG. 2. Percentage of original yield of aqueous POE xanthate (POEX6), prepared at pH 8, as a function of pH as determined by UV-visible spectroscopy.

TABLE 4. Characteristics of POEX and PMMAX

Experiment	Oxidizer	$\langle M \rangle$, g · mol ⁻¹	UV abs. peaks, nm	UV abs. peak ratio
POEX-:		$\langle M_w \rangle$		
1	I ₂	3,600	—	—
2	I ₂	4,600	—	—
3	I ₂	20,800	—	—
4	I ₂	41,000	—	—
5	(NH ₄) ₂ S ₂ O ₈	94,000	287/239	0.52
6	(NH ₄) ₂ S ₂ O ₈	118,000	287/239	0.52
PMMAX-:		$\langle M_n \rangle$		
1	I ₂	7,150	—	—
2	I ₂	9,750	—	—

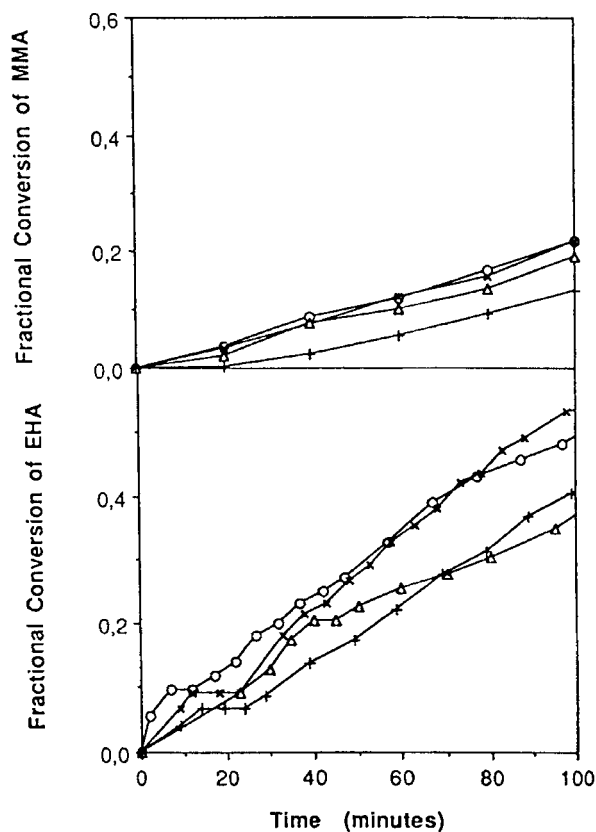


FIG. 3. Fractional conversion of MMA and EHA for experiments M1 and E1 (○), M2 and E2 (×), M3 and E3 (△), and M4 and E4 (+). M1, M2, M3, M4, E1, E2, E3, and E4 are described in Table 3.

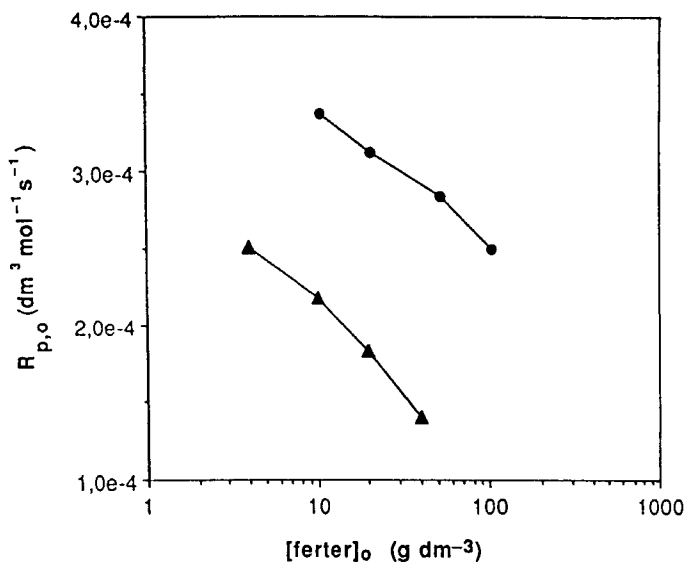


FIG. 4. The initial rates of polymerization, $R_{p,0}$, as a function of initial ferter concentrations, $[\text{ferter}]_0$, for the MMA (●) and EHA (▲) polymerizations.

spectroscopy. In general, the weight-average M values, $\langle M_w \rangle$, were used to find the relative degree of coupling of a ferter. In the case of PMMAX, however, the number-average molecular weight, $\langle M_n \rangle$, was more appropriate for this purpose, as the coupling reaction was predominantly between the small, relatively mobile xanthate species at the high polymer concentrations used for the reaction ($\sim 30\%$). The purity of the POEX product could be gauged by observing: 1) the location of two peak maxima, which for pure diethyl dixanthogen are 237 and 286 nm; 2) the absorbance ratio of these two peaks $-\epsilon(\lambda = 237 \text{ nm})/\epsilon(\lambda = 286 \text{ nm}) \cong 0.52$; and 3) the qualitative features of its UV spectrum between 200 and 400 nm, since the UV spectra of unreacted xanthate and typical by-products of the oxidation (e.g., perxanthate ion, R-OCSSO^- , and monothiocarbonate ion, R-OCSO^-) could readily be distinguished from dixanthogen [8, 9]. For PMMAX, the strongly absorbing acrylate moiety masks most of the spectrum of dixanthogen, and only the dixanthogen peak at around 286 nm could be positively identified. UV-visible spectroscopy was not appropriate for monitoring the success of oxidation in the case of I_2 oxidations since I_2 absorbs strongly in the same wavelength region as dixanthogen and it was difficult to remove all traces of I_2 .

Iodine is a popular and effective agent for the coupling of xanthates in low-polarity media, and its performance in the present study appeared to be adequate. Oxidation in the aqueous phase was carried out using peroxodisulfate. The oxidation with peroxodisulfate produced high molecular weight polymer with few apparent side reactions. Jones and Woodcock also found that peroxodisulfate was an effective oxidizer for aqueous ethyl xanthate [9].

TABLE 5. Number- and Weight-Average Molecular Weight versus Time and Fractional Conversion for the Polymerization of MMA in the Presence of POEX3

Experiment	Time, min	(a) x_{MMA} , % ^a	$\langle M_w \rangle / 10^5$, g · mol ⁻¹	$\langle M_n \rangle / 10^5$, g · mol ⁻¹
M1	20	3.7	8.86	4.64
	40	8.6	10.32	7.08
	60	12.0	11.79	7.35
	80	16.7	12.73	7.11
	100	21.7	14.36	6.35
M2	20	3.4	10.28	7.67
	40	7.3	14.41	10.43
	60	12.2	9.06	5.23
	80	15.6	10.45	5.43
	100	21.8	13.31	7.52
M3	20	2.2	4.03	1.97
	40	7.6	6.72	4.39
	60	10.0	8.16	4.82
	80	13.6	9.00	5.70
	100	18.9	10.7	6.29
M4	20	0.3	—	—
	40	2.5	2.98	1.49
	60	5.6	7.13	4.65
	80	9.2	7.55	3.52
	100	13.1	8.5	4.29

^aFraction conversion of MMA.

Block Copolymerization

The ability of dixanthogen to act as a ferter in a free-radical polymerization is already established albeit for slightly different systems. In order to test the chain transfer and termination properties of the present ferters, one can study the initial rate of polymerization, $R_{p,0}$, as a function of initial ferter concentration, $[\text{ferter}]_0$. If $R_{p,0}$ decreases with increasing $[\text{ferter}]_0$, then it is usually inferred that there is greater termination due to the high chain transfer activity of the ferter. RO (C=S)S radical generated by chain transfer reaction may also be stable enough to reduce the rate of the reinitiation step and to decrease the rate of polymerization. Indeed, the time-conversion curves for the polymerizations of MMA and EHA (Fig. 3) in the presence of POEX and PMMAX, respectively, and the corresponding curves representing $R_{p,0}$ versus $[\text{ferter}]_0$ (Fig. 4) indicate that both POEX and PMMAX act as ferters. Further evidence that POEX undergoes significant transfer is given by the decreasing $\langle M_n \rangle$ values with increasing concentration of POEX (Table 5).

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