One-Step, One-Pot Photoinitiation of Free Radical and Free Radical Promoted Cationic Polymerizations

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ABSTRACT: We describe here a novel approach to photoinitiate free radical and cationic polymerizations concurrently, involving the use of benzoin in conjunction with an onium salt such as diphenyl iodonium or N-alkoxy pyridinium salt. On photolysis, benzoyl radicals formed from the decomposition of benzoin initiate free radical polymerization of methyl methacrylate. The hydroxy benzyl radicals formed concomitantly are readily oxidized to the corresponding cation by the onium salt to initiate cationic polymerization of cyclohexene oxide in the same system. Evidence for two independent polymerizations was obtained from studies involving gel permeation chromatography, extractions, and infrared and proton nuclear magnetic resonance analysis of the polymers. The effect of the type of the onium salt on each polymerization was also investigated. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2389–2395, 2002

Key words: one-step, one-pot photoinitiation; free radical polymerization; cationic polymerization; electron transfer; onium salt

INTRODUCTION

One-step, one pot methodlogy has recently been introduced to the synthetic polymer chemistry as an elegant way to prepare block copolymers from monomers that polymerize by different mechanisms.[1–5] In this concept, bifunctional intiators containing different reactive sites initiate two different polymerizations independently in a sequential or simultaneous manner according to the following scheme.

Important requirements for the success of such systems are that any step of each polymerization should not interfere with any other step and that both polymerizations should be compatible. Recently, several examples involving different polymerization mechanisms employed in a one-pot, one step concept have been reported, and corresponding block copolymers were prepared in a straightforward manner. Puts and Sogah[1] suc-cessfully prepared block and graft copolymers of vinyl pyridine, styrene, and 2-oxazolines by one-step, one-pot initiation of cationic- and nitroxide-mediated living radical polymerization. The amphiphilic polymers were also prepared from the hydrolysis of the oxazoline and styrene block copolymers obtained according to this procedure.[4] Recently Hawker et al.[5] reported dual living polymerizations from a single initiating molecule without a requirement of additional reaction. The compatibility of either stable free radical-mediated or atom transfer living-radical polymerization with living-ring opening polymerization of ϵ-caprolactone was demonstrated by the synthesis of a variety of well-defined block copolymers.

During the last two decades, photoinitiated polymerization have received considerable attention and have been practically applied in a variety of areas, including printing inks, adhesives, surface coating, microelectronics, and printing plates.[6] Photoinitiated polymerization can be conducted by both radical and cationic means. In addition to the widely employed photoinitiated free radical polymerization, the corresponding cationic poly-
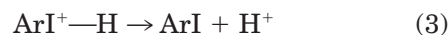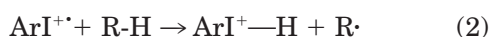
Sequential

Similtaneous
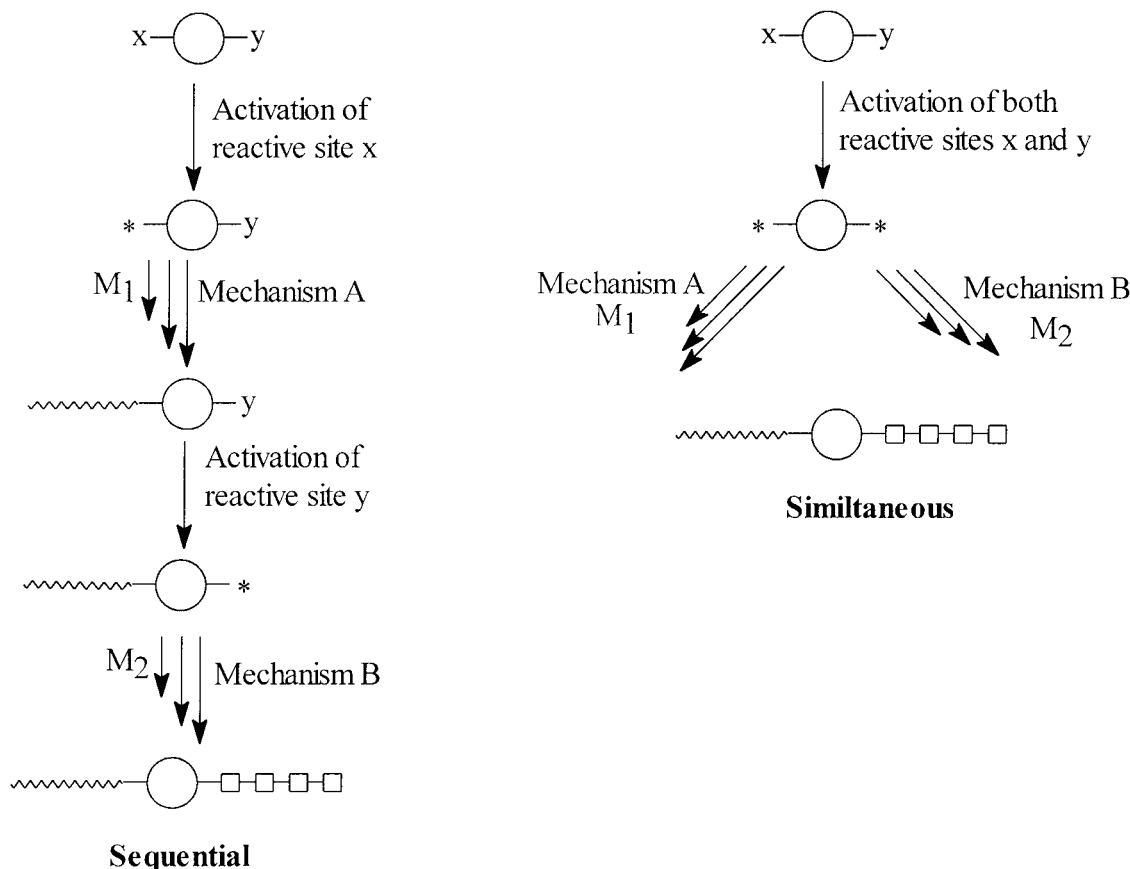
Scheme 1   One-pot, one-step intiation of two different polymerizations.

merization has also gained importance after the discovery by Crivello of onium salts as highly photosensitive and efficient cationic photoinitiators.[7] Thermally stable onium-type photoinitiators include diaryl iodonium,[8] triaryl sulphonium,[9] and alkoxy pyridinium salts[10,11] with nonnucleophilic counter ions such as AsF_6^-, SbF_6^-, BF_4^-, and PF_6^-.

$$Ar_2I^+X^- \qquad Ar_3S^+X^- \qquad \text{OR} \quad X^-$$

$$X^- = AsF_6^-, SbF_6^-, BF_4^- \text{ and } PF_6^-$$
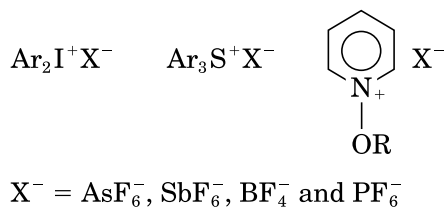
Irradiation of these salts results in the formation of reactive cations (or Brønsted acids) as shown in the example of iodonium salts.

$$Ar_2I^+ \xrightarrow{h\nu} ArI^{+\cdot} + Ar\cdot \qquad (1)$$

$$ArI^{+\cdot} + R\text{-}H \rightarrow ArI^+\text{—}H + R\cdot \qquad (2)$$

$$ArI^+\text{—}H \rightarrow ArI + H^+ \qquad (3)$$

As it is obvious from reactions 1–3, concurrent radical polymerization, initiated by aryl and alkyl radicals, and cationic polymerization, initiated by aryl iodonium radical cations and/or Brønsted acids, can proceed. Application of such hybrid systems in ultraviolet (UV) curable formulations containing bifunctional crosslinkable monomer components has been described.[12] To the best of our knowledge, however, there has been no report on the use such a hybrid initiating system for the preparation of linear polymers.

Certain onium salts such as diphenyl iodonium[13,14] and alkoxy pyrdinium[15] salts may be used to oxidize photochemically generated electron-donating free radicals according to reaction (4), thus generating reactive cations.

$$(4)$$
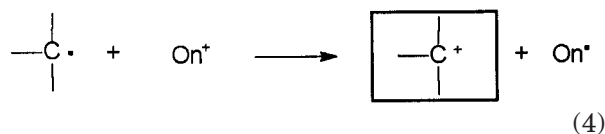
This so-called free radical-promoted cationic polymerization is an elegant and fairly flexible
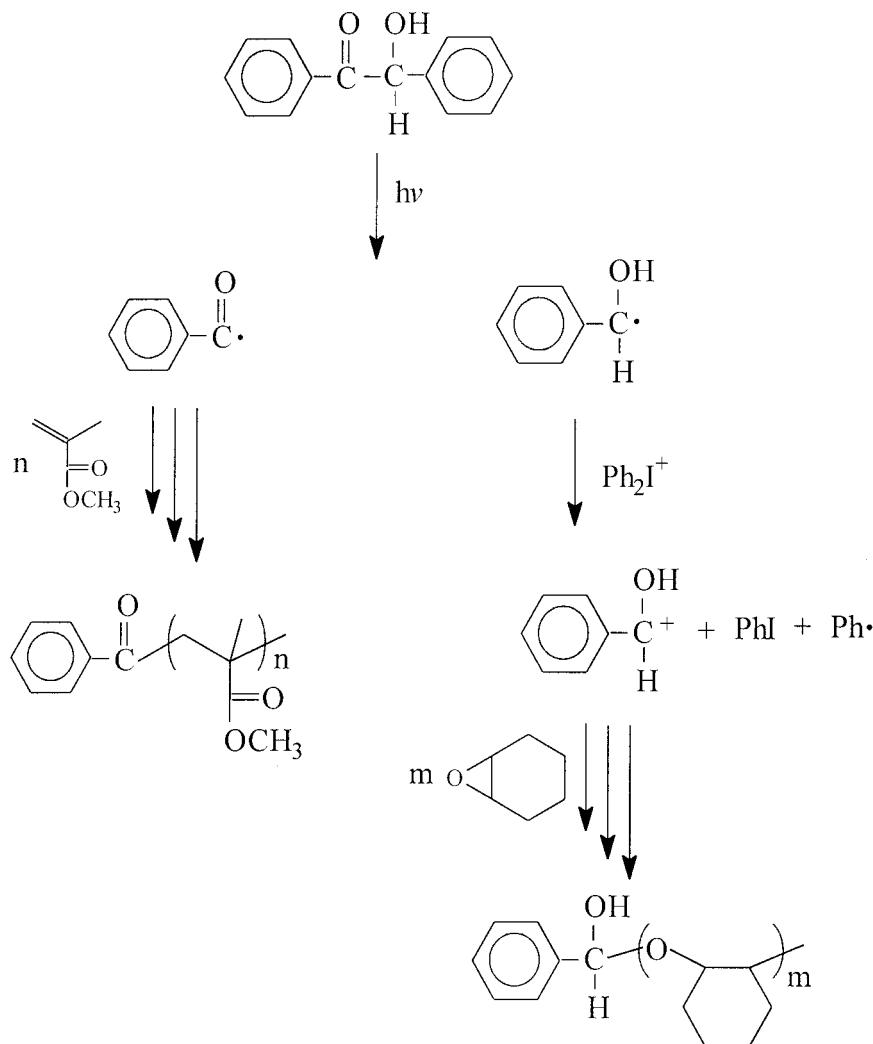
Scheme 2 One-pot, one-step photoinitiation of free radical and free radical promoted cationic polymerizations.

way to extend the spectral response of onium salts to a 300–400-nm region. The aim of this article is to report the use of an α-clevage type photoinitior such as benzoin in free radical and free radical-promoted cationic polymerizations that facilitate the similtaneous photoinduced synthesis of poly(cyclohexene oxide) (PCHO) and poly(methyl methacrylate) (PMMA) in a one-pot, one-step process.

EXPERIMENTAL

Materials

Benzoin (B) (Aldrich) was recrystalized from ethanol. Cyclohexene oxide (CHO) (Aldrich, Deisenhofen, Germany) was vacuum distilled from calcium hydride (CaH$_2$) before use. Methyl methac-

rylate (MMA) (Aldrich) was washed with 5% aq. NaOH solution, dried over CaCl$_2$, and vacuum distilled from CaH$_2$. Dichloromethane (CH$_2$Cl$_2$) (Lab-

Table I   One-Pot, One-Step Photoinitiated Polymerization of Cyclohexane Oxide (CHO) and Methyl Methacrylate (MMA) in CH$_2$Cl$_2$ at Room Temperature under 350 nm Irradiation

Code	[Ph$_2$I$^+$PF$_6$] (mol/L)	Overall Conversion (%)	Mn $\times$ 10^{-3}	Mw/Mn
1	5×10^{-4}	10	5.7	5.0
2	2×10^{-3}	38	3.8	3.6
3	5×10^{-3}	52	2.7	2.1
4	7×10^{-3}	57	2.7	1.5

[Benzoin] $= 5 \times 10^{-3}$ mol/L, [CHO] $= 3.3$ mol/L, [MMA] $= 3.1$ mol/L, time of irradiation $= 60$ min.

Table II   Seperation of Poly(Cyclohexene Oxide) (PCHO) and Poly(Methyl Methacrylate) (PMMA) and Molecular Weights

Code	PCHO Fraction[a]			PMMA Fraction[b]		
	(%)	$Mn^c \times 10^{-3}$	Mw/Mn	(%)	$Mn^c \times 10^{-3}$	Mw/Mn
1	40	2.2	1.25	60	41	2.1
2	64	2.9	1.6	36	32	3.0
3	74	3.4	1.7	26	25	2.5
4	76	2.8	1.6	24	28	2.6

[a] n-Hexane soluble part.
[b] n-Hexane insoluble part.
[c] Determined by gel permeation chromatography according to polystyrene standards.

scan) (Amsterdam, The Netherlands) was washed with concentrated H_2SO_4 until the acid layer remained colorless, then washed with water, aq. %5 NaOH, and then water again. It was predried with $CaCl_2$ and distilled from CaH_2. Diphenyliodonium hexafluorophosphate[8] ($Ph_2I^+PF_6^-$), triphenylsulfonium hexafluorophosphate[9] ($Ph_3S^+PF_6^-$), and N-ethoxy-2-methylpyridinium hexafluorophosphate[11] ($EMP^+PF_6^-$), were prepared as described previously.[16]
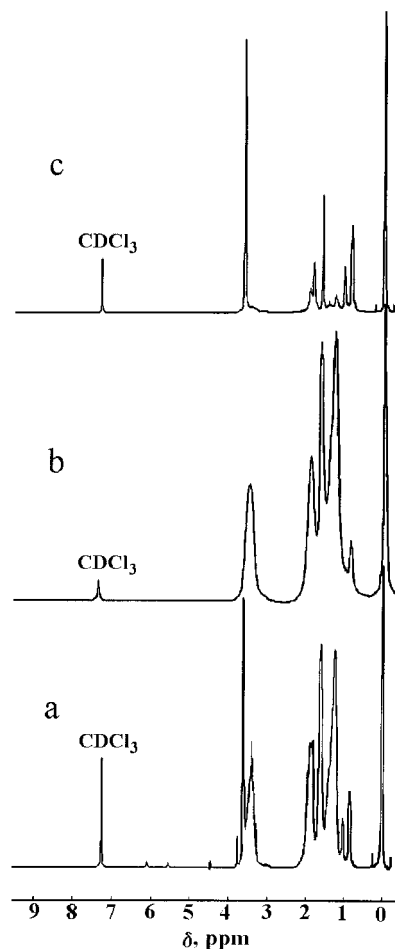
Photopolymerization

Appropriate solutions of monomer mixtures (CHO and MMA) in dichloromethane containing benzoin and onium salt (EMP^+ or Ph_2I^+ or Ph_3S^+) in Pyrex tubes were degassed with nitrogen before irradiation. At the end of irradiation in a merry-go-round-type photoreactor equipped with 15 Philips lamps and emitting light nominally at 350 nm at room temperature, the solutions were poured into methanol. The precipitated polymers were filtered off and dried *in vacuo*. Conversions were determined gravimetrically. Light intensity was measured by an Aberchrome actinometer and found to be $6.12 \ 10^{-5}$ Einstein s^{-1}.

Characterization of Polymers

Polymers obtained as described above were subjected to extraction with n-hexane. This way, homopolymers were successfully seperated, as n-hexane is solvent for homopoly(cyclohexene oxide) and nonsolvent for homopoly(methyl methacrylate). Gel permeation chromatography (GPC) chromatograms were obtained by using a Waters instrument equipped with a R410 differential refractometer and 600E pump and with THF as the eluent, at a flow rate of 1.0 mL/min. Molecular weights were calculated by using monodisperse

polystyrene standards. Proton nuclear magnetic resonance (^{1}H-NMR) measurements were performed in $CDCl_3$ solution using a Bruker 250 MHz instrument. UV spectra were recorded on a

Figure 1 Proton nuclear magnetic resonance spectra of the polymerization product (a); and n-hexane soluble part (b) and insoluble part (c).
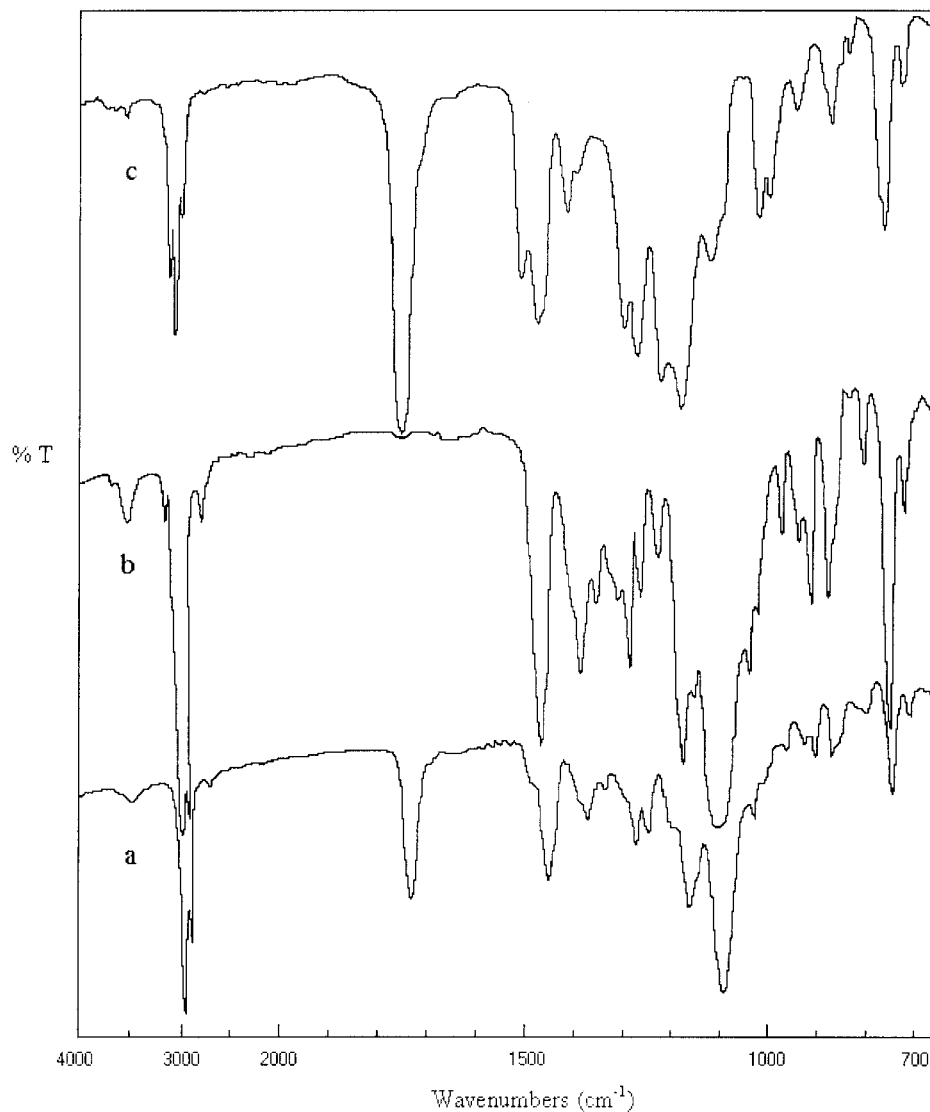
Figure 2 Infrared spectra of the polymerization product (a); and n-hexane soluble part (b) and insoluble part (c).

Perkin-Elmer Lambda spectrophotometer (Uber-lingen, Germany). The infrared (IR) spectra were recorded on a Shimadzu IR-470 infrared spectrophotometer (Kyoto, Japan).

RESULTS AND DISCUSSION

MMA and CHO were delibarately chosen as free radical and cationic polymerizable monomers, respectively. For structural reasons, MMA polymerizes only by radical and anionic mechanisms. However, CHO polymerizes only by cationic mechanism and is unreactive toward photochemically generated radicals. It is, therefore, expected that the polymerization of either monomer is not influenced by the other monomer. As they are photolized with fairly high quantum yields, benzoin and derivatives are so far the most effective photoinitiators.[17] The photolysis of benzoin results in α-clevage and hydroxybenzyl (strong electron donor), and benzoyl (electron withdrawing) radicals are formed, as shown in eq. (5).

(5)
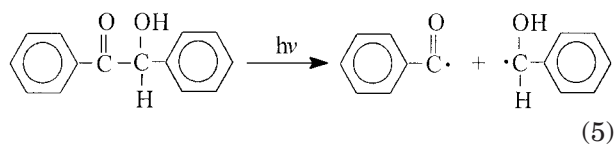
When irradiated in the presence of an onium salts such as diphenyl iodonium or N-ethoxy-2-

methyl pyridinium salts at waveleghts where onium salt is transparent, the light is absorbed only by benzoin.[11,13]

The photochemically generated hydroxy benzyl radicals reduce the iodonium salt to yield corresponding carbocations capable of initiating cationic polymerization of CHO. The influence of factors, such as light intensity, onium salt concentration, or type of radical source on the rate of radical induced cationic polymerization with benzoin derivative/onium salt systems has been carefully investigated.[18] The benzoyl radicals formed concominantly initiate the polymerization of MMA. The overall mechanism is represented in Scheme 2.

Tables I and II summarizes the data obtained for the polymerization and extraction experiments. The data in Table I reveal that the overall conversion increased with the iodonium salt concentration. The composition of the polymerization products is shown in Table II. Interestingly, the PCHO content in the mixture initially increased and remained constant with increasing iodonium salt concentration. This is expected to occur, because phenyl radicals stemming from the iodonium salt decompostion can contribute to the further polymerization of MMA.

Evidence for the independent processes of free radical and free radical-promoted cationic polymerization can be obtained from the spectral and GPC analysis of the polymerization products. For example, the ^{1}H-NMR spectrum of the mixture obtained from the polymerization in Figure 1(a) represents resonance peaks of the both homopolymers. However, the spectrum of the n-hexane soluble and insoluble parts clearly show resonances characteristics of homopoly(cyclohexene oxide) and homopolymethyl methacrylate at 4.3 and 4.1 ppm, respectively [Fig. 1(b,c)].

The IR spectra of the mixture and n-hexane extraction products, which are shown in Figure 2, strongly support the efficiency of one-pot, one-set photoinitiation of free radical and cationic polymerizations. For example, the IR spectra of the soluble and insoluble parts show absorption peaks at 1046 cm^{-1} because of ether groups and at 1739 cm^{-1} because of carbonyl groups of PCHO and PMMA, respectively [Fig. 2(b,c)]. Notably, both absorptions appear in the spectrum of the mixture before n-hexane treatment [Fig. 2(a)]. The GPC traces of the polymerization products are shown in Figure 3. The trace a is for the crude product after polymerization, and the traces b and c are for n-hexane soluble and insoluble parts. The molecular weight distribution of the
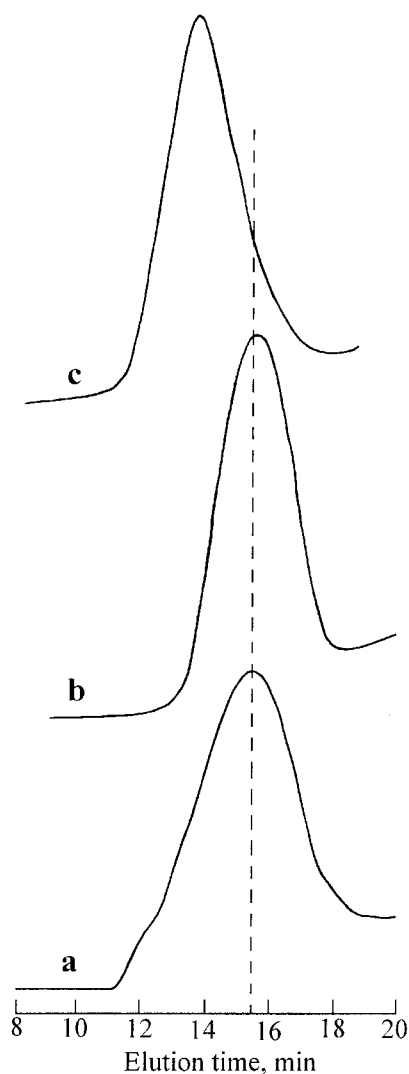
Figure 3 Gel permeation chromatography traces of the polymerization product (a); and n-hexane soluble part (b) and insoluble part (c).

polymerization product [Fig. 3(a)] is rather broad. After extraction, both homopolymers have a narrower molecular weight distribution. The relatively narrow distribution of PCHO [Fig. 3(b)] indicates more controlled polymerization in the cationic route. In fact, this behavior is observed in all cases.

The efficiency of onium salts as oxidizing agents is related to their electron affinity.[19] The higher the oxidation power of the onium salt, the higher (more positive) the reduction potential $E_{1/2}^{red}$ (On$^+$). As can be seen from Table III, iodonium salt is the most powerful oxidation agent that contributes to the higher overall and CHO conversions. Triphenylsulphonium salt does not participate in such electron transfer processes be-

Table III   Effect of the Type of Onium Salt on One-Pot, One-Step Polymerizations of Cyclohexane Oxide and Methyl Methacrylate[a]

				Composition of the Mixture[b]	
Code	Onium Salt	$E_{red}^{1/2}$ V(SCE)	Conversion (%)	PCHO (%)	PMMA (%)
3	Ph_2I^+	-0.2^{20}	52	74	26
5	EMP^+	-0.7^{11}	9	40	60
6	Ph_3S^+	-1.2^{21}	8	—[c]	>98

[a] [Benzoin] = 5×10^{-3} mol/L, [Onium salt] = 5×10^{-3} mol/L, [CHO] = 3.3 mol/L, [MMA] = 3.1 mol/L, time of irradiation = 60 min; PCHO = polycyclohexane oxide), PMMA = poly(methyl methacrylate).
[b] Determined by extraction with n-hexane.
[c] On pouring into methanol, no precipitation but turbidity occurred.

cause of an unfavorable redox potential. In this case, cationic polymerization does not proceed. Thus, under these conditions, only PMMA is formed via free radical polymerization initiated by radicals formed from benzoin. The intermediate behavior of the pyridinium salt is also related to its redox potential.

In conclusion, CHO and MMA can be polymerized simultaneously in a one-pot, one-step manner by photolysis of benzoin in the presence of an oxidizing onium salt. One of the two radicals thus formed initiates the free radical polymerization, whereas the other undergoes an electron transfer reaction to initiate the cationic polymerization. The percentage of each polymer can be adjusted by the type and concentration of the onium salt used as the oxidizing agent in the system. The advantage of this approach is the possibility of simultaneous preparation block copolymers by using cyclic or main-chain polymeric benzoin photoinitiators. Further studies in this line are now in progress and will be reported elsewhere.

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