Block Copolymers by Combination of Radical and Promoted Cationic Polymerization Routes

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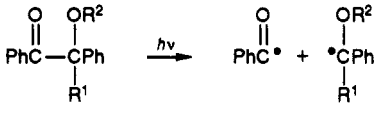
ABSTRACT: A block copolymer of cyclohexene oxide and styrene was prepared by using bifunctional azobenzoin initiators via a two-step procedure. The functionality of the initiator pertains to thermally degradable azo group and thermally stable photoactive benzoin groups. In the first step, thermal polymerization of styrene using azobenzoin initiators was carried out to yield polymers with photoactive end groups. These prepolymers were used to induce polymerization of cyclohexene oxide through formation of electron donor macroradicals upon photolysis and subsequent oxidation to corresponding carbocations in the presence of 1-ethoxy-2-methylpyridinium hexafluorophosphate resulting in the formation of a block copolymer. A different sequence of the same procedure was also employed. Successful blocking has been confirmed by a strong change in the molecular weight of the prepolymer and the block copolymer as well as IR and NMR spectral measurements.

Introduction

Block copolymers have recently attracted a revitalized interest because of their unique and novel properties. Various methods to synthesize these polymers have been known for a long time. However, these methods are limited to certain types of monomers and exclude other monomers that polymerize by other mechanisms. Richard[1,2] was the first to propose a general method that allows multiple combinations of monomers. In this approach, polymer A, prepared by one mechanism, is terminally functionalized, isolated, and subsequently used to initiate the polymerization of a second monomer, by a different mechanism, to form block copolymers. Recently, we have described[3-10] the preparation of block copolymers using functional azo initiators as polymerization transformation agents.

Benzoin (B) and its derivatives are extensively used[11] because of their ability to initiate free radical polymerization of vinyl monomers. Upon irradiation in the 300–400-nm range, these compounds undergo scission with high quantum efficiencies according to the following reaction.

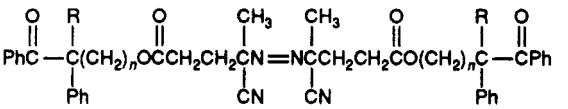


(1)

R^1 = H, alkyl, substituted alkyl
R^2 = H, alkyl, substituted alkyl

Smets[12,13] incorporated benzoin methyl ether (BME) groups into polycarbonate by performing the polycondensation of bisphenol A with phosgene in the presence of 4,4′-dihydroxybenzoin methyl ether. Upon UV irradiation of the resulting polycondensate in the presence of methyl methacrylate (MMA), a block copolymer was formed.

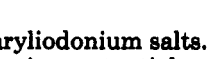
Quite recently, we have used[14-16] a similar approach to prepare block copolymers of vinyl monomers with the aid of azobenzoin initiators of the following structures.



ACPB: R = H, n = 0
ABME: R = OCH_3, n = 1

These bifunctional low molar mass initiators contain two chromophoric groups, namely, azo and benzoin groups, that differ significantly in thermal activity and photoactivity. The most effective use of these initiators can be made by thermolysis of the azo groups in the presence of monomer A and subsequent photolysis of the benzoin groups in the presence of monomer B. Since the benzoin moieties are contained as terminal groups in the polymer formed in the first step, a block copolymer can be formed in the second step. It was found that the efficiency of the block copolymerization greatly depends on the kinetic behavior of the radically polymerizable monomer involved in the photochemical step.[16]

It was shown[17] that the oxidation of electron donor radicals to corresponding carbocations may conveniently be used to promote cationic polymerization of compounds such as epoxides, cyclic ethers, and alkyl vinyl ethers. The overall process may be represented by reaction 2 and useful



(2)

oxidants include diaryliodonium salts. Pyridinium salts of appropriate reduction potential are also capable of participating in similar redox reactions.[18]

In the present work, azobenzoin initiators were used as a free radical source to produce benzoin-terminated polymers. Irradiation of these polymers in conjunction with onium salts in the presence of cyclohexene oxide (CHO) as a cationically polymerizable monomer makes it possible to synthesize block copolymers of monomers of different chemical nature.

Experimental Section

Materials. Styrene (St), cyclohexene oxide (CHO), and solvents were purified by conventional drying and distillation

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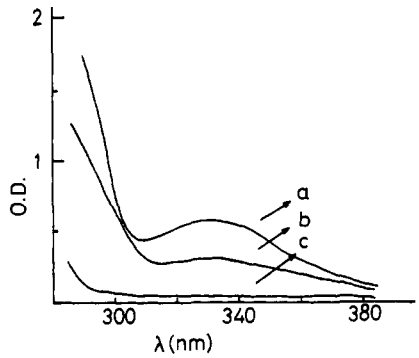


Figure 1. Optical absorption spectra of (a) BME, (b) ABME, and (c) $EMP^+PF_6^-$ at 5×10^{-4} mol/L concentration in dichloromethane.

Table I
Polymerization of Styrene Initiated by ABME[a]

code	10^3[I], mol/L	temp, °C	time, min	conv, %	M_n[b]
PST1	15	80	150	33.90	35 400
PST2	1	70	240	7.91	94 000
PST3	5	60	120	4.77	130 400

[a] [M] = 8.71 mol/L. [b] Number-average molecular weight; determined by GPC.

procedures. *O,O'*-[Azobis(4-cyano-1-oxo-4,1-pentanediyl)]bis(benzoin) (ACPB) and α,α'-[azobis(4-cyano-1-oxo-4,1-pentanediyl)oxymethylene]bis(benzoin)dimethyl ether (ABME) were prepared as described previously.[14] 1-Ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$) was prepared according to a procedure described by Reichard.[19] Diphenyliodonium hexafluorophosphate and triphenylsulfonium hexafluorophosphate were prepared according to the published methods.[20,21]

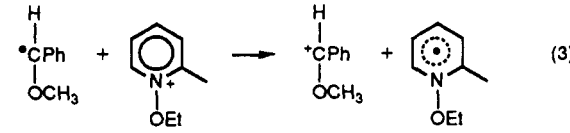
Preparation of Photoactive Polystyrene. Bulk styrene (St) containing a known amount of ABME in Pyrex tubes was degassed in a vacuum system. For polymerization, the tubes were immersed in a constant-temperature bath. At the end of a given time the reaction mixtures were poured into a 10-fold excess of methanol and the precipitated polymers were filtered off. Polymers were then purified by dissolving in methylene chloride and precipitating into methanol before use in photopolymerization experiments.

Promoted Cationic Block Copolymerization. Prior to irradiation on a Rayonet merry-go-round photoreactor equipped with lamps emitting light at nominally 350 nm, argon was bubbled through the solutions of CHO in dichloromethane containing onium salt and photoactivator. A phenanthrene solution (10^{-2} mol/L) in *n*-hexane was used as a filter throughout the work in order to prevent direct absorption by the onium salts.

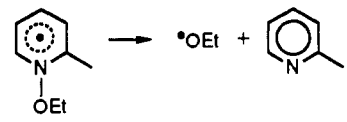
Characterization of Polymers. Polymers formed during irradiation were separated from the reaction mixture by precipitation into methanol. Homopoly(cyclohexene oxide) was extracted with *n*-hexane. GPC chromatograms were obtained by using a Knauer M64 instrument equipped with a differential refractometer using THF as the eluent at a flow rate of 1 mL/min. Molecular weights were calculated by using polystyrene standards. ^1H NMR spectra were taken on a Brüker 200 spectrometer in $CDCl_3$ solution with tetramethylsilane as internal standard. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer in film on KBr disks. UV spectra were recorded on a Shimadzu UV-160 spectrophotometer.

Results and Discussion

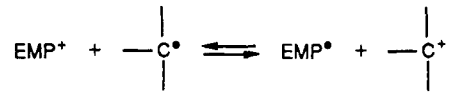
Figure 1 shows optical absorption spectra of $EMP^+PF_6^-$ and BME-type photoactivators used in this study. Since the pyridinium salt does not absorb at 350 nm, all irradiations were performed at 350 nm by the use of a filter solution. As can be seen from Table II, CHO was polymerized quite effectively by using low molar mass benzoin derivatives as free radical sources. It is assumed that in the system under consideration, the alkoxyalkyl radical, which was formed upon irradiation according to reaction 3, acts as a fairly powerful reducing agent.


(3)

The pyridinyl radical formed in this way is very short lived.[18] Its decomposition according to reaction 4 occurs very rapidly. On this basis, EMP^+ was expected to be


(4)

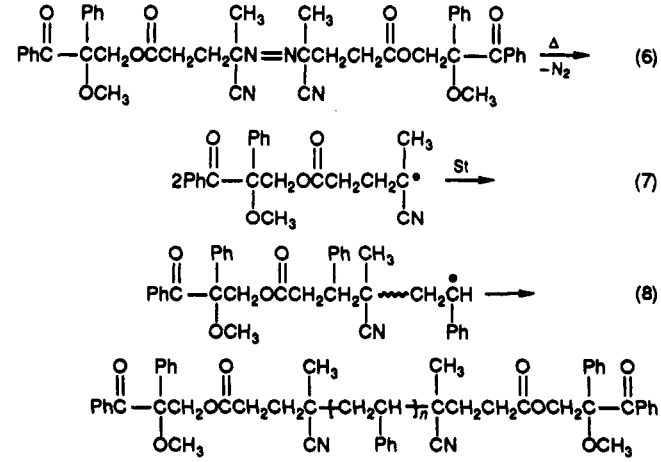
quite appropriate for the generation of carbocations via reaction with electron-donating radicals, because the occurrence of back reactions in this process can be excluded.


(5)

Benzoin proved to be a less efficient photoactivator than benzoin methyl ether for the promoted cationic polymerization of CHO (see Table II). This implies that the methoxybenzyl radical has a higher reducing power than the hydroxybenzyl radical. Different reactivities of the corresponding cations toward CHO may also contribute to the initiation efficiency. In ABME-promoted cationic polymerizations, the iodonium salt appeared to be the most efficient onium salt. This behavior may be attributed to the tail absorbtion of the iodonium salt. Under these conditions direct initiation by the iodonium salt to some extent cannot be prevented.

A different situation was encountered in the case of the triphenylsulfonium salt. These salts are not capable of initiating the free radical promoted cationic polymerization; this can be explained in terms of the quite different redox potentials (relative to SCE) of the three salts: −1.2 V (Ph_3S^+),[22] −0.2 V (Ph_2I^+),[23] and −0.7 V (EMP^+).[18]

As stated previously, our main interest is in the block copolymerization of CHO with vinyl polymers. In order to be used in block copolymerization experiments, polystyrenes of various molecular weights, possessing benzoin methyl ether groups, were prepared (Table I) according to the following sequence of reactions.


(6)

(7)

(8)

Table II
Promoted Cationic Polymerization of CHO Using Low Molar Mass Photoactivators in CH_2Cl_2[a]

run	photoactivator, 5×10^{-3} mol/L	onium salt, 5×10^{-3} mol/L	conv, %
1	B	EMP^+	18.83
2	BME	EMP^+	40.73
3	ABME	EMP^+	28.49
4	ABME	Ph_2I^+	33.48
5	ABME	Ph_3S^+	0

[a] λ = 350 nm; [M] = 5.90 mol/L; time = 30 min.

Table III
Promoted Photopolymerization of CHO Using BME-Terminated Polystyrene in CH_2Cl_2[a]

photoactive polymer (g/L)	conv, %	comp of reaction mixture		comp of block copolymer	
		PCHO, %	PSt-*b*-PCHO, %	PSt, %	PCHO, %
PSt1 (13.33)	19.60	82.89	17.11	81.66	22.51
PSt2 (13.33)	6.20	61.12	38.88	83.20	16.82
PSt3 (13.33)	8.30	76.52	23.48	85.32	14.67
PSt1 (26.66)	8.50	53.26	46.74	88.11	11.85

[a] λ = 350 nm; [M] = 5.90 mol/L; [EMP^+] = 5×10^{-3} mol/L; time = 30 min.

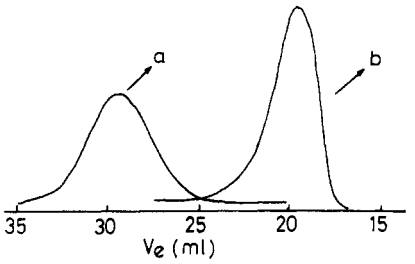
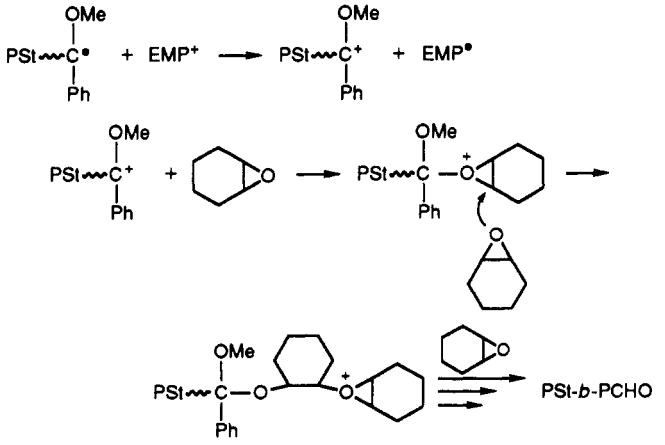


Figure 2. GPC chromatograms recorded with (a) prepoly(cyclohexene oxide) containing azo groups and (b) the block copolymer of cyclohexene oxide and styrene after extraction with *n*-hexane.

Details of the kinetics and mechanisms of the polymerization of St initiated by the thermolysis of these type of initiators were reported previously.[15,16] UV irradiation of the resulting prepolymers caused α-scission and yielded benzoyl radicals and polymer-bound radicals.

If the photolysis is carried out in the presence of CHO and EMP^+, the polystyrene-attached radical is converted to the initiating cations to generate block copolymers.



Typical results concerning block copolymerization are presented in Table III. As can be seen both the molecular weight and the concentration of photoactive PSt affect the conversion, block yield, and composition of the block copolymer.

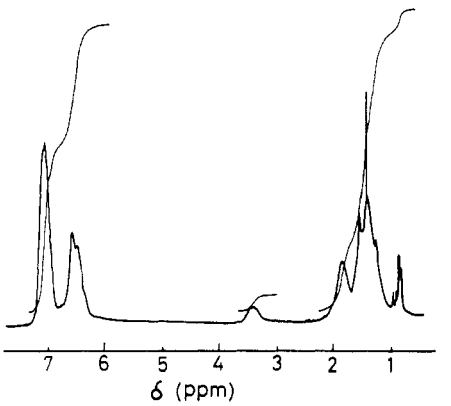
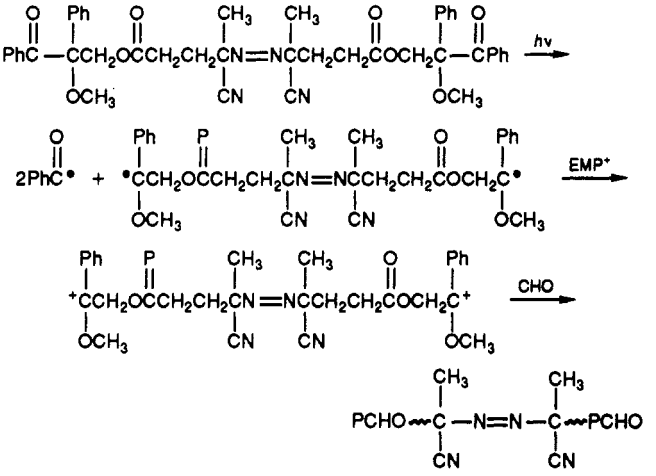


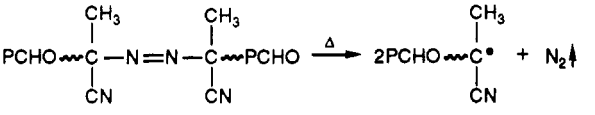
Figure 3. NMR spectrum of the block copolymer of styrene and cyclohexene oxide after extraction with *n*-hexane in $CDCl_3$.

A different sequence of the same procedure may also be used. Photoinitiated polymerization of CHO using ABME in conjunction with EMP^+ provided the formation of PCHO possessing an azo linkage in the main chain. At the irradiation wavelength (λ = 350 nm), most of the emitted light was absorbed by benzoin methyl ether chromophoric groups ($\epsilon \cong 225$), since the azo group has a relatively weak absorption ($\epsilon \cong 20$).



PCHO functionalized in this way will decompose on heating and forms two radicals in a similar way to AIBN.

If the thermolysis is carried out in the presence of a free



radical polymerizable monomer such as St, the PCHO-attached radical may initiate free radical polymerization to generate a copolymer. As an experimental demonstration, PCHO (obtained from run 3, in Table II) was used to initiate the polymerization of St. Bulk St containing 35 g/L PCHO heated at 60 °C for 8 h yielded a 6% overall conversion of St. A control experiment in the absence of the initiator gave about 1% conversion of St after the same reaction time. Efficiency of azo-linked PCHO as a free radical initiator is not optimized in any way since each polymer chain contains one functionality and can produce only two polymeric radicals. The type of the block copolymer depends greatly on the kinetic behavior of the particular monomer involved. Initiation of St polymerization by means of azo-linked PCHO is expected to yield a PCHO unit at each and since

termination is by radical–radical combination. Figure 2 shows the GPC chromatograms of azo-linked PCHO and block copolymer after extraction with *n*-hexane. The new peak at higher molecular weight is ascribed to the block copolymer. The block copolymer structure was also assigned by means of IR and NMR spectral measurements. The IR spectra of purified block copolymer show the characteristic ether bond of the PCHO segment at 1090 cm^{-1} in addition to the usual PSt bands. The NMR spectrum of the block copolymer displays signals at 0.8–2.2 ppm CH_2, CH (PSt, PCHO), 3–3.6 ppm OCH (PCHO), and 6.5–7.2 ppm Ph (PSt) (Figure 3).

In conclusion, block copolymerization via promoted cationic and radical routes provides a versatile two-stage method applicable to nucleophilic and vinyl monomers. In principle, it should not matter which route is employed first. It is clear that this procedure can be used to prepare AB- and ABA-type block copolymers according to the kinetic behavior of the free radical polymerizable monomer involved.

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Registry No. B, 119-53-9; ABME, 131301-13-8; EMP+PF_6, 30927-77-6; St, 100-42-5; CHO, 286-20-4; Ph_2I^+, 58109-40-3; BME, 3524-62-7; (CHO)(St) (block copolymer), 134111-46-9.