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Synthesis of block copolymers by transformation of photosensitized cationic polymerization to stable free radical polymerization

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Abstract

Anthracene-photosensitized cationic polymerization of cyclohexene oxide at $\lambda = 350$ nm in conjuction with onium salts, namely *N*-ethoxy-2-methyl pyridinium hexafluorophosphate ($EMP^+PF_6^-$) or diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$), in the presence of a stable radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), yielded polymers with alkoxyamine terminal groups. These polymers were found to be efficient initiators for stable free radical polymerization (SFRP) of styrene. IR, ^{1}H-NMR spectral analysis and GPC studies of the obtained polymers show that block copolymers are readily formed as a result of combination of photosensitized cationic and stable free radical polymerization mechanisms. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Transformation reactions; Photosensitized cationic polymerization; Stable free radical polymerization

1. Introduction

The various methods have been proposed and used for the synthesis of block copolymers [1]. Among them the transformation approach is an elegant way to cover a wide range of monomer combinations [2,3]. Transformation reactions involve synthesis in which two (or more) mutually exclusive polymerization mechanisms are sequentially combined. The transformation approach, comprises different propagating species and allows multiple combination of monomers. In this approach monomer 1 is polymerized by a mechanism 'A' to produce a polymer with a functional group F that is capable of initiating polymerization by a different mode/mechanism 'B' (Scheme 1).

Many examples concerning the use of transformation reactions in block copolymers were reported by us and others [1,3].

N-alkoxy pyridinium salts are effective initiators for the cationic polymerization of cyclic ethers such as cyclohexene oxide and vinyl ethers such as *n*-butyl vinyl ether [4]. Their photoactivity can be tuned to a broad wavelength range by the use of free radical sources [5], charge transfer complexes [6] and photosensitizers [7].

Photosensitized cationic polymerization attracted particular interest since the triggering of the initiation may be extended to much longer wavelengths, where pyridinium salts are transparent and photosensitizers such as anthracene, perylene and phenothiazines absorb the light. The electron transfer mechanism has been postulated as demonstrated for the case of anthracene photosensitizer [7] (Scheme 2)

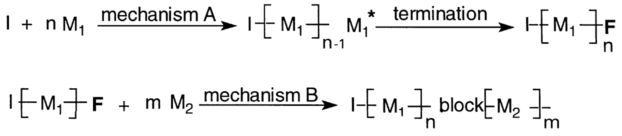
Controlled ''stable free radical polymerization'' (SFRP) has recently been a study of increasing interest [8,9]. This type polymerization can be realized through reversible deactivation of growing radicals by stable radical such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (Scheme 3).

In the present work, a block copolymer of cyclohexene oxide (CHO) and styrene (St) was prepared by sequential polymerization of photosensitized cationic polymerization and stable free radical polymerization.

2. Experimental

2.1. Materials

Dichloromethane (CH_2Cl_2), styrene (St) and cyclohexene



Scheme 1. Transformation reactions.

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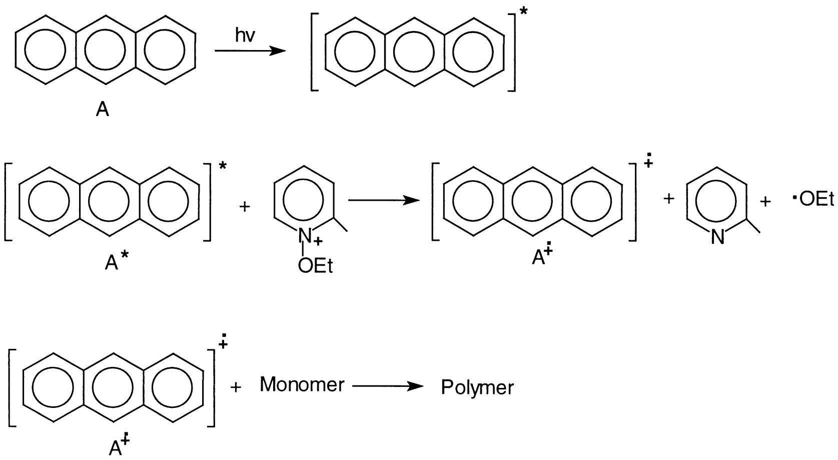
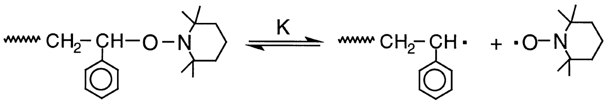


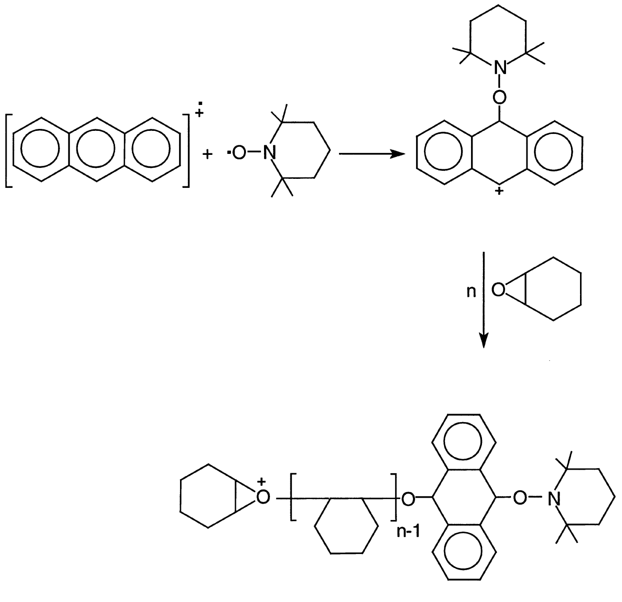
Scheme 2. The action of anthracene as a photosensitizer for the initiation of the polymerization in conjuction with $EMP^+PF_6^-$.

oxide (CHO) were purified by conventional drying and distillation procedures.

N-Ethoxy-2-methyl pyridinium hexafluorophosphate ($EMP^+PF_6^-$) was prepared according to a procedure described by Reichardt [10]. Diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) was prepared as described previously [11]. Anthracene (Merck) was purified by sublimation. 2,2,6,6-Tetramethyl-1-piperidinyl-1-oxy (TEMPO) (Aldrich) was used without further purification.



Scheme 3. Reversible termination of growing free-radical chains by using a stable free radical.

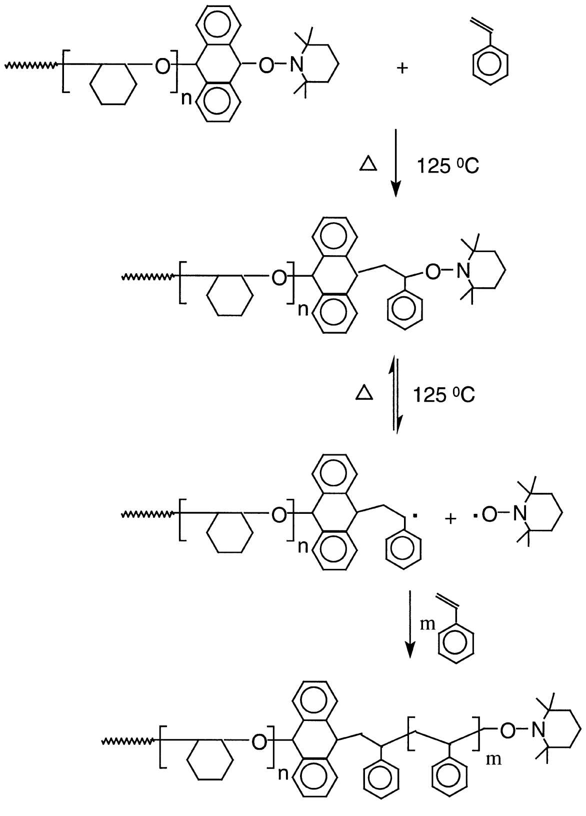


Scheme 4. Photosensitized cationic polymerization of cyclohexene oxide in the presence of TEMPO.

$$Ph^{\bullet}\ (EtO^{\bullet}) + R\text{-}H \longrightarrow Ph\text{-}H + (EtOH) + R^{\bullet}$$

$$R^{\bullet} \xrightarrow{On^{+}} R^{+}$$

Scheme 5. Cation generation from radicals.



Scheme 6. Bulk block copolymerization of cyclohexene oxide and styrene.

Table 1
Photosensitized polymerization[a] of cyclohexene oxide in the presence of TEMPO in metylene chloride

Code	$EMP^+PF_6^- \times (10^3)$ (mol/l)	$Ph_2I^+PF_6^- \times (10^3)$ (mol/l)	Irradiation time (min.)	Postpolym.time[c] (h)	Conversion(%)	M_n[b] $\times (10^{-3})$	M_w/M_n
PCHO-1	7	—	90	—	10.3	3.2	1.5
PCHO-2	7	—	180	—	16	2.9	2.5
PCHO-3	—	7	90	—	17.5	3.1	2.6
PCHO-4	7	—	90	24	41.8	3.5	2.6

[a] [Anthracene] = 5×10^{-3} mol/l, [Cyclohexeneoxide] = 6.58 mol/l, [TEMPO] = 2×10^{-2}mol/l, $\lambda = 350$ nm.

[b] Number avarege molecular weights were determined by GPC according to polystyrene standards.

[c] Kept at room temperature in dark.

Table 2
Block copolymerization[a] of poly(cyclohexene oxide) with styrene

Code	Prepolymer(g/l)	[PCHO]/[St] × (10^4) (mol/mol)	Time (h)	Conversion(%)	M_n[b] × (10^{-3})	M_w/M_n
PCHO-St 1	(PCHO-1) (26)	6.3	20	75	40	1.5
PCHO-St 2	(PCHO-4) (19)	6.3	15	41	22	1.58
Control	(PCHO-0)[c]	6.3	1.8	28	26	1.95

[a] [Styrene] = 8.73 mol/l, [TEMPO] = 1.6 × 10^{-2}mol/l, Temperature = 125°C.

[b] Number average molecular weights were determined by GPC according to polystyrene standards.

[c] Poly(cyclohexene oxide) without TEMPO moieties.

2.2. Preparation of poly(cyclohexene oxide)(PCHO) having TEMPO moiety

Solutions of CHO in dichloromethane, in pyrex tubes, containing onium salts ($EMP^+PF_6^-$ or $Ph_2I^+PF_6^-$), and anthracene as a photosensitizer in the presence of excess TEMPO, were deaerated by bubling with nitrogen and subsequently irradiated on a monochromator at 350 nm. After a given time, solution poured into methanol, the precipitated polymer was filtered off and dried in vacuo.

2.3. Block copolymerization of St by using PCHO as a macroinitiator

Above obtained PCHO macroinitiator and St were put into a tube. The tube was degassed and sealed under nitrogen prior to placement into thermostatically controlled bath at 125°C. At the end of a given time, the reaction mixture was poured into methanol and the precipitated polymer was filtered off and dried in vacuo.The crude polymer was extracted with *n*-hexane (solvent for homopoly(cyclohexene oxide).

3. Results and discussion

Photosensitized cationic polymerization of CHO by using anthracene and two different onium salts, namely, *N*-ethoxy-2-methyl pyridinium hexafluorophosphate (EMP^+PF_6) or diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$), redox couples were performed in the presence of TEMPO (Table 1).

Previously [12], poly(tetrahydrofuran) with anthracene terminal units were employed to elucidate the mechanism of photoinitiation in these system. Formation of block copolymers and UV spectral analysis revealed that anthracene radical cations react with ethoxyl radicals steming from the decomposition of $EMP^\cdot$ radicals. By utilizing TEMPO in the photosensitized polymerization, alkoxyamine with TEMPO coupled to poly(cyclohexene oxide) was synthesized. Electron transfer between anthracene and onium salt yields anthracene radical cations which are quickly trapped by the nitroxide radicals to give consequently alkoxyamine functional dihydroanthryl cations capable of initiating cationic polymerization of CHO as depicted in Scheme 4.

It is worth noting that with Ph_2I^+ salt higher polymer yields are obtained. This reflects their readiness to act as electron acceptors since the reduction potential of diphenyliodonium ions are thermodynamically more favorable ($E^{1/2}_{\text{red for }Ph_2I^+} = -0.2\text{V}\ E^{1/2}_{\text{red for EMP}^+} = -0.7\text{V}$) [13,6].

It is also interesting to note that in the absence TEMPO conversion to PCHO is higher. This was attributed to the participation of radicals formed from the decomposition of onium salts, i.e phenyl and ethoxy radicals, in further cation generation process by hydrogen abstraction and electron transfer reactions according to the following reactions (Scheme 5).

Subsequently, bulk polymerization of styrene using the

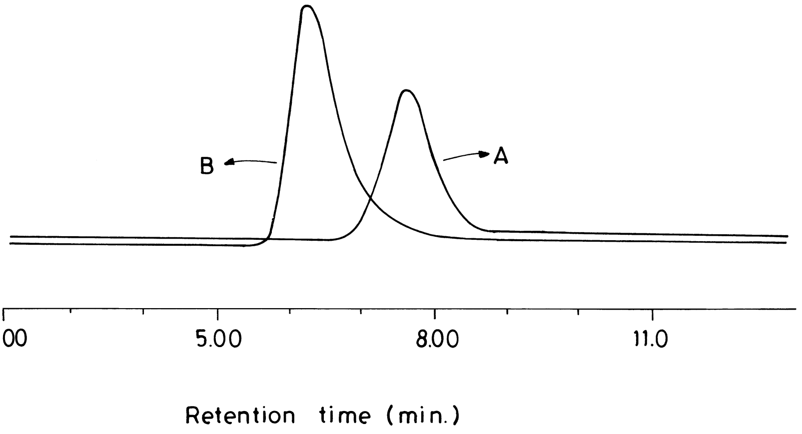


Fig. 1. GPC traces of (A) PCHO macroinitiator (PCHO-1) and (B) block copolymer (PCHO–PSt1).

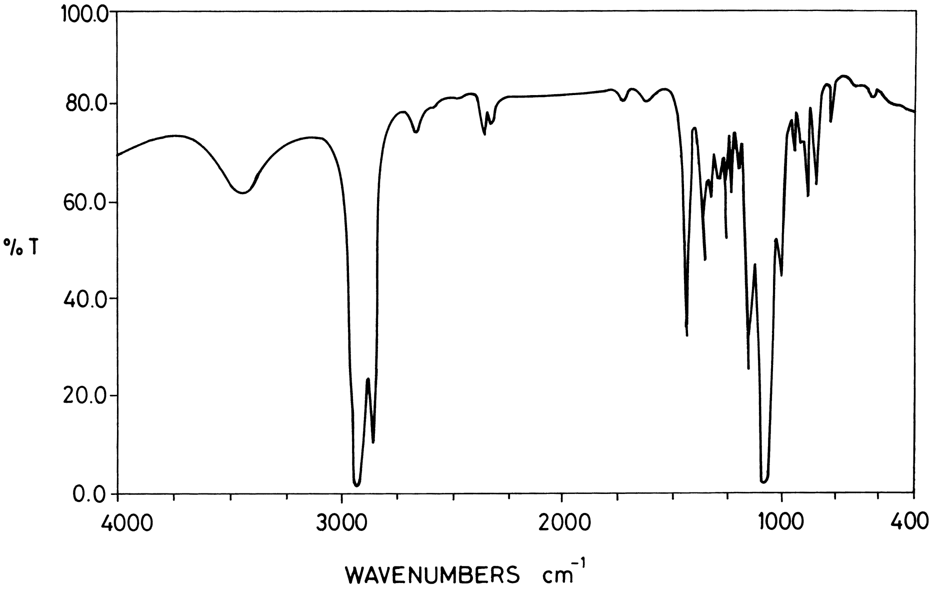


Fig. 2. IR spectrum of PCHO macroinitiator (PCHO-1).

PCHO obtained previously was carried out at 125°C. The results are shown Table 2 along with that of the control experiment. It should be pointed out that much faster polymerization and higher molecular weight distribution were observed with the non-functionalized PCHO.

Similar to previous report [14], alkoxyamine terminated polymers were used successfully as a polymeric initiator for SFRP of styrene to afford block copolymers. Mechanism of block copolymerization is shown in Scheme 6.

Fig.1 shows the GPC traces of alkoxyamine terminated PCHO and block copolymer. The new peak at higher molecular weight is ascribed to the block copolymer. Homo PCHO was able to be seperated from the block polymer by hexane extraction since it is solvent for PCHO but non-solvent for PS. However, both the weight and GPC trace did not change by the extraction. The block copolymer structure was also assigned by means of IR and ^{1}H-NMR spectral measurements. The IR spectra of block copolymer shows the characteristic ether bond of the PCHO segment at 1100 cm^{-1}, in addition to the usual PSt bonds, i.e. 1600 cm^{-1} (Figs. 2 and 3). The ^{1}H-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) (Fig. 4). The unit ratio of the St to CHO were

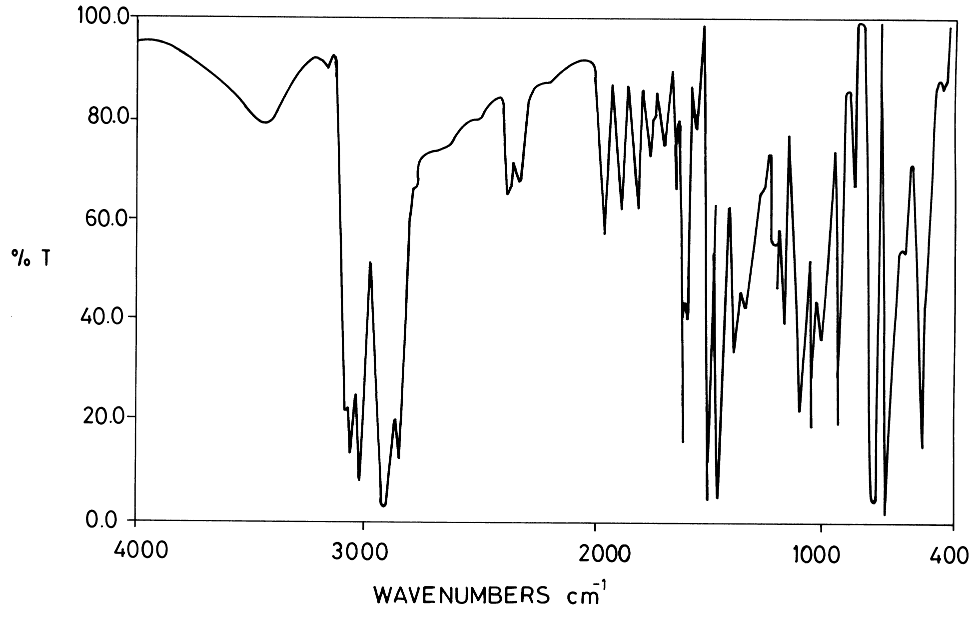


Fig. 3. IR spectrum of block copolymer (PCHO–PSt1).

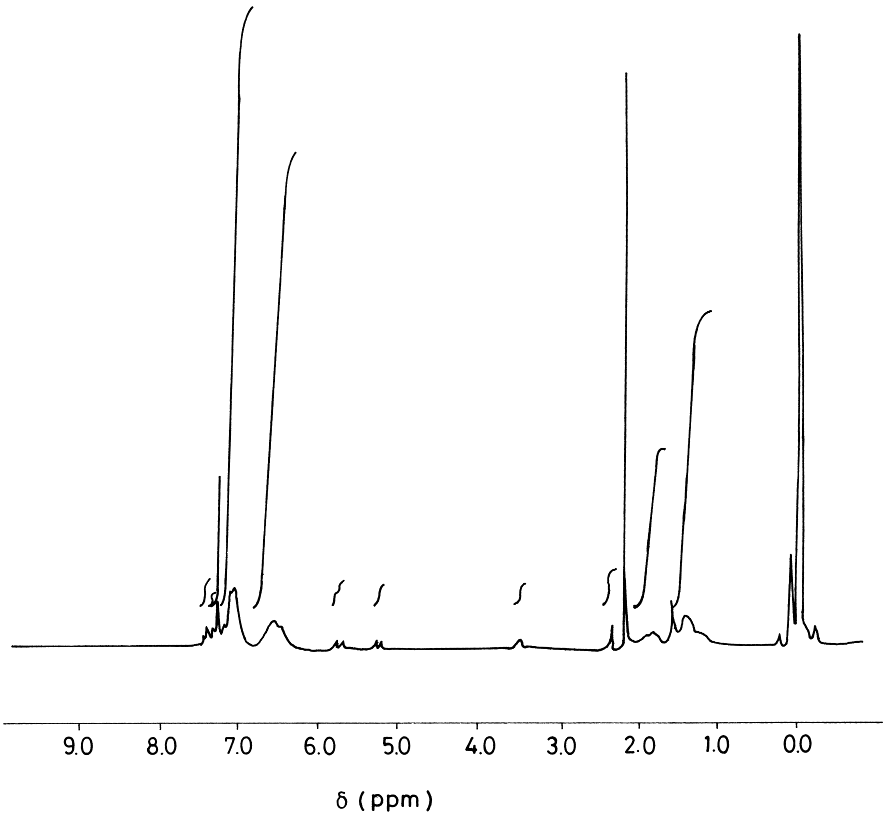


Fig. 4. ^{1}H-NMR spectrum of block copolymer (PCHO–PSt1).

determined as 18 : 1 by ^{1}H-NMR from the integration ratios of aromatic protons to etheric protons and as 11 : 1 by GPC measurements. The discrepancy may be because of the difference of the hydrodynamic volumes of both segments.

In conclusion, block copolymerization via combination of photosensitized cationic and SFRP routes provides a versatile two-stage method applicable to cyclic ethers and styrene monomers.

Acknowledgements

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