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BLOCK COPOLYMERIZATION OF VINYL MONOMERS WITH MACROPHOTOINIFERTER

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ABSTRACT

Macrophotoiniferter, α-(diethyldithiocarbamylacetyl)-ω-(diethyldithiocarbamylacetoxy)-poly(ethylene glycol), was synthesized and block copolymers were prepared by the photopolymerizations of styrene, methyl methacrylate, butyl acrylate, and vinyl acetate, vinyl monomers initiated with it. The mechanism of vinyl polymerization was investigated by ESR technique and diethyldithiocarbamyl end group analysis of macrophotoiniferter. The results indicated that block copolymers of poly(ethylene glycol) and vinyl polymer were obtained. NMR and GPC were used to characterize the block copolymers.

INTRODUCTION

Block copolymers with hydrophilic and hydrophobic segments, such as polyethylene glycol and polystyrene, find potential application as stabilizers of aqueous dispersions. In aqueous emulsion polymerization they can act as surface-active materials. Besides anionic living polymerization, these block copolymers can be synthesized using the combination of ionic—radical polymerization[1, 2]. The polymer prepared by one mechanism is terminally functionalized, separated, and subsequently used to initiate a second monomer to polymerize by a different mechanism. Polyethylene glycol with hydroxyl group was often prepared by anionic polymerization of ethylene oxide and its hydroxyl group can be transfered to thiuram disulfide group to form thermal macroiniferter. It can initiate the radical polymerization of vinyl monomers to form block copolymers[3], [4] . Ethyl diethyldithiocarbamylacetate was found to be used as a photoiniferter[5] and its structure is similar to the polyethylene glycol with diethyldithiocarbamyl end group.

This paper describes the synthesis and the characterization of macrophotoiniferter containing diethyldithiocarbamyl end group on polyethylene glycol,i.e.,α-(diethyldithiocarbamylacetyl)-ω-(diethyldithiocarbamylacetoxy)-poly(ethylene glycol), represented as PEG-I. Block copolymers consist of vinyl polymers with polyethylene glycol were synthesized by photopolymerization of vinyl monomers in the presence of PEG-I.

EXPERIMENTAL

Material: Commercial polyethylene glycol (PEG, M_n 3100), sodium diethyldithiocarbamate trihydrate, 2-methyl-2-nitrosopropane (MNP) from Aldrich Company were used as received. Styrene (St), methyl methacrylate (MMA), butyl acrylate (BA), and vinyl acetate (VAc) were purified by vacuum distillation. Benzene, acetic anhydride, pyridine, tetrahydrofuran(THF), acetonitrile, and benzoyl chloride were distilled. Acetic acid was recrystallized twice from benzene, mp: 62-64°C. Sodium hydroxide and sodium bicarbonate were used without purified. Chloroacetyl chloride was prepared by the reaction of benzoyl chloride and acetic acid, bp: 105-107°C.

Synthesis of Macrophotoiniferters (PEG-I): PEG (18 g), chloroacetyl chloride (2.7 mL), and benzene (100 mL) were refluxed for 20 hours under nitrogen. The excess chloroacetyl chloride and benzene were removed under vacuum. The residual of PEG was completely washed by diethyl ether and dried under vacuum. The resulting PEG derivative reacted with sodium diethyldithiocarbamate trihydrate (5.8 g) in 150 mL anhydrous ethanol, refluxed for 5 hours and stirred overnight at room temperature, filtrated, and removed ethanol under vacuum. The residual solid PEG-I was dissolved in benzene and precipitated into cold petroleum ether. PEG-I was characterized by IR, NMR, UV, and GPC spectroscopies.

ESR Study: The activity of Et_2NCSS end group under UV light was investigated by spin trapping and ESR technique using MNP as trapping agent. The solution of sample (0.5 mL 0.1g/mL) in benzene and MNP (0.04 mL 0.2 *M*) in acetonitrile in a flat quartz tube was irridiated and ESR spectrum was recorded on a Bruker ER 200D-SRC electron spin resonance spectrometer using the TM cavity at the X-band with 12.5 KHz modulation and 1.00 mW microwave power.

Block copolymerizations of vinyl monomers with PEG-I: PEG-I (0.5 g) , monomers(St 0.55 mL, MMA 0.54 mL, BA 0.56 mL) and benzene (1.0 mL) or acetonitrile (3.0 mL) were polymerized under irradiation of UV light with an 80-W UV lamp at 10 cm from sealed glass tubes at room temperature for 12-20 hours. The reaction product was washed by petroleum ether to removed the monomers and dried under vacuum. The separation of polymers into homopolymers and block polymers was carried out by extraction with suitable solvents, PEG-I with anhydrous ethanol, PS with cyclohexane, PMMA and PBA with acetone, and PVAc with methanol. Then the fractions were examined by IR and ^{1}HNMR spectra and GPC analysis, respectively.

Measurement: GPC was carried out by Waters 208 instrument equipped with a differential refractometer and Styragel 50nm columns using tetrahydrofuran as eluent, and calibration with polystyrene standards. The values of number average molecular weights of PEG and PEG-I were 3.11×10^3 and 3.25×10^3, respectively. UV spectroscopy was recorded on Shimadzu UV-250 and UV-2100 instrument. IR and ^{1}HNMR spectra were recorded on Nicolet IR 750 spectrometer and Bruker ARX 400 spectrometer, respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization of Macrophotoiniferter (PEG-I)

The synthesis of macrophotoiniferter (PEG-I) was described in experimental and it was characterized by ^{1}HNMR spectrum shown in Fig. 1. From which 4.17 ppm ($O{=}CCH_2SSCNEt_2$), 3.99 and 3.80 ppm [$SSCN(CH_2CH_3)_2$], and 1.27 ppm [$SSCN(CH_2CH_3)_2$] are observed, respectively. The number of end group (Et_2NCSS) of PEG-I was determinated to be 1.82 by UV spectroscopy, using ethyl diethyldithiocarbamylacetate as standard (λ_{max}=280 nm)[5].

Mechanism of Block Copolymerization in the Presence of PEG-I

It was found that S-S bond of thiuram disulfide in a thermal iniferter cleaved irreversibly to form radical $R_2NCSS\bullet$ in thermal polymerization, which slowly initiated polymerization and rapidly scaveaged growing radicals to produce dithiocarbamyl end group[3]. The dithiocarbamyl group was quite thermally stable but cleaved homolytically in the UV light and photochemical cleavage of C-S bond in dithiocarbamyl group may provide reversible systems to control the photopolymerization of vinyl monomer[5]-[8] . PEG-I can form macroradicals 1 and radical $Et_2NCSS\bullet$ under UV light due to their end groups being similar with ethyl diethyldithiocarbamylacetate, which is a photoiniferter[5], as shown in Scheme 1. The adduct of macroradical 1 with MNP is radical 3 (a_α^N=14.2G, a_β^H =7.7G) which is observed by ESR spectrum in Fig. 2. From which it can be seen that the other radical (a_α^N =15.6G) is the adduct of MNP and radical $(CH_3)_3C\bullet$, which is formed by the photolysis of MNP itself under UV light.

Radical 1 can initiate vinyl monomer polymerization and radical $Et_2NCSS\bullet$ may reversibly react with growing radical to control the chain length. PEG-I with about two Et_2NCSS end group will form radicals at two end of chain. Thus, block copolymers of ABA type shall be predominantly prepared by the photopolymerizations of vinyl monomers in the presence of PEG-I.

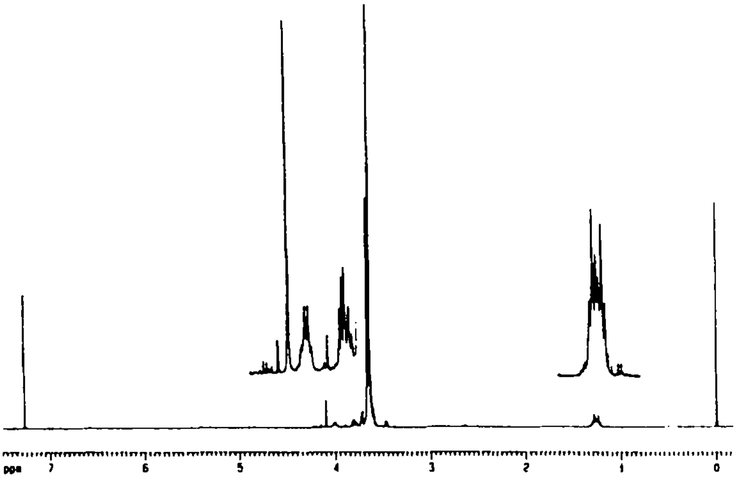
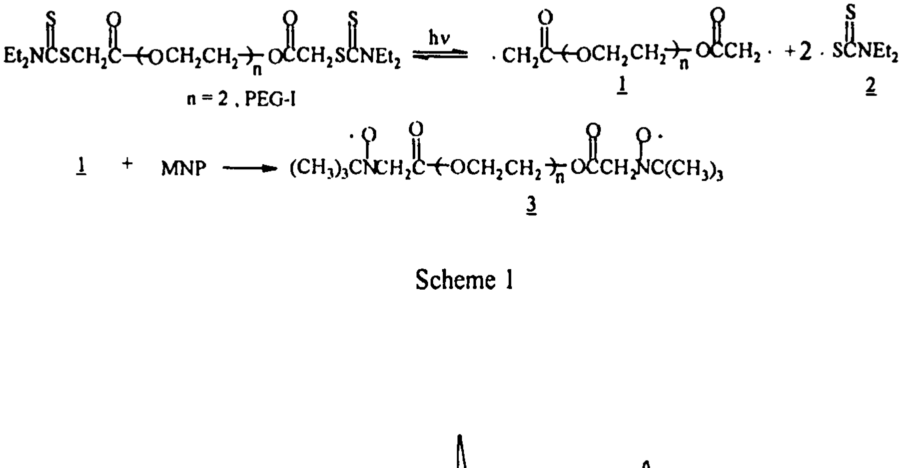


Fig. 1 ^{1}HNMR spectra of PEG-I in CDCl$_3$.



$$Et_2N\overset{S}{\overset{\|}{C}}SCH_2\overset{O}{\overset{\|}{C}}\text{-}(OCH_2CH_2)_n\text{-}O\overset{O}{\overset{\|}{C}}CH_2S\overset{S}{\overset{\|}{C}}NEt_2 \xrightarrow{h\nu} \cdot CH_2\overset{O}{\overset{\|}{C}}(OCH_2CH_2)_nO\overset{O}{\overset{\|}{C}}CH_2\cdot + 2\cdot S\overset{S}{\overset{\|}{C}}NEt_2$$

n = 2, PEG-I; 1; 2

$$1 + MNP \longrightarrow (CH_3)_3C\overset{\cdot O}{N}CH_2\overset{O}{\overset{\|}{C}}(OCH_2CH_2)_nO\overset{O}{\overset{\|}{C}}CH_2\overset{O\cdot}{N}C(CH_3)_3$$

3

Scheme 1

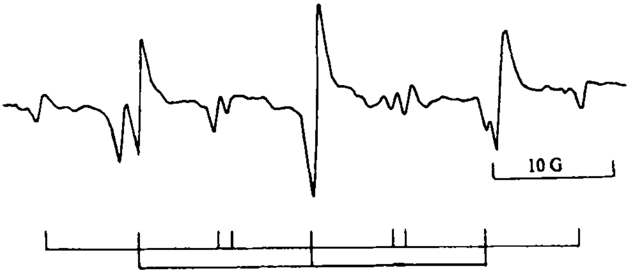


Fig. 2 ESR spectrum of PEG-I/MNP system (1mT=10G): [PEG-I]= 0.08 g/mL, [MNP]= 3.9×10^{-3}*M*.

Table 1

Block copolymerization of second monomers(M) with PEG-I

No.	PEG-I	M	t	P_{total}	Block		copolymer	
	(g)	(mL)	(hr)	(g)	(g)	M block(wt%)	M_n (10^{-4})	M_w/M_n
1	0.499	St 0.55	20	0.536	0.397	24.9	0.433	2.61
3	0.502	MMA 0.54	12	0.674	0.404	41.4	0.555	2.07
6	0.207	VAc 1.10	10	0.422	0.181	5.52	0.344	3.21
7	0.502	BA 0.56	12	0.878	0.447	26.6	0.443	2.84

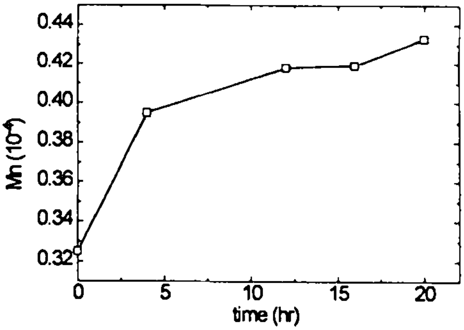


Fig. 3 The time–M_n relation for block copolymerization of St with PEG-I.

Synthesis and Characterization of Block Copolymers

The photopolymerizations of vinyl monomers (St, MMA, BA, and VAc) were carried out in the presence of PEG-I. Block copolymers were obtained after purifed and the result was listed in Table 1. From which it can be seen that the molecular weights of block copolymers are larger than original polymers (PEG-I, $M_n = 3.25\times10^3$). In the photopolymerization of St with PEG-I molecular weights of block copolymers were observed to increase with reaction time as shown in Fig.3, and the values of M_w/M_n were around 2.9—2.6.

The resulting block copolymers were charaterized by NMR and UV spectroscopies. From the ^{1}HNMR spectra of vinyl polymer-PEG block copolymers, besides the chemical shift of 3.65 ($-CH_2O$) for PEG, 3.60 ($-OCH_3$) and 1.01 [$-CH_2-C(COOCH_3)(CH_3)-$] forPMMA, 4.03 [$-CH_2-CH(CO_2C_4H_9)-$] and 0.94 (CH_3 in butyl) for PBA, and 4.87 [$CH_2-CH(O_2CCH3)-$] 2.04(CH_3COO-) for PVAc were observed, respectively. PS-PEG block copolymer was confirmed by the UV spectroscopy, from which a new peak at λ_{max} = 260 nm was observed. It revealed the presence of phenyl group of PS in the block copolymer. The result indicated that the block copolymers had been synthesized.

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