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A novel macroinimer of polyethylene oxide: synthesis of hyper branched networks by photoinduced H-abstraction process

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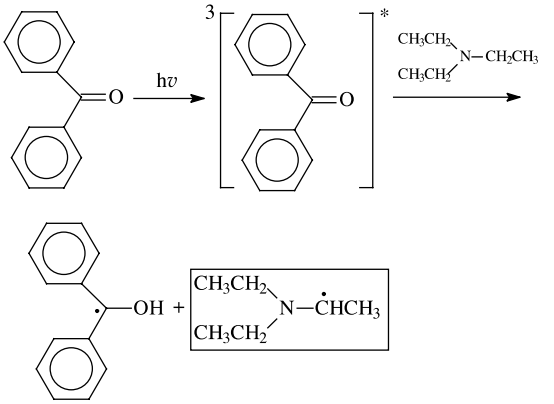
Abstract

A novel poly(ethylene oxide) macroinimer (PEO-macronimer) possesing methacryloyl and tertiary amino end groups was prepared by ring-opening polymerization of ethylene oxide initiated by potassium 2-methylaminoethoxide and termination of living ends of PEO with methacryloyl chloride. NMR analysis showed that the macronimer contains equal amount of amino and methacrolyl groups indicating efficient initiation and termination processes. The dimethylamine end group in conjunction with benzophenone under UV irradiation produced ternary amine methylene radicals via H-abstraction mechanism which initiates the polymerization. Photopolymerization in solutions at high macroinimer concentration or in films resulted in the formation of insoluble networks. The crosslinked polymers exhibit high swelling capacity in organic solvents and water due to the hyperbranched nature.

Keywords: Macroinimer; Poly(ethylene oxide); Photoinduced polymerization; H-abstraction; Hyper branched networks

1. Introduction

The most effective light induced radical generation processes used in polymer synthesis are α-cleavage reactions and hydrogen abstraction reactions [1–3]. The latter are particularly useful when the hydrogen donating groups incorporated into chain ends and side chains. Radicals are generated in a bimolecular process by the reduction of a photoexcited aromatic carbonyl compound by hydrogen abstraction as illustrated below for the case of the benzophenone/triethylamine photoinitiating system [4,5].



The radicals formed on the amino group are considered as the initiating radicals while ketyl radicals were demonstrated to undergo radical coupling. Selective and

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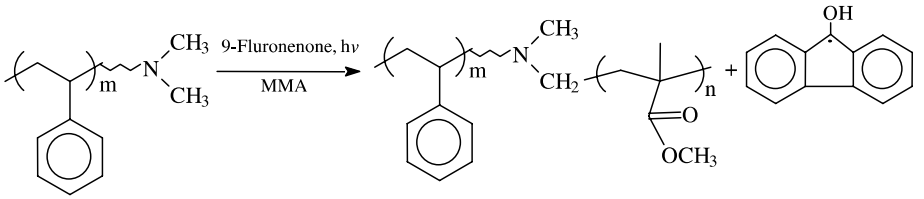
efficient formation of block and graft copolymers may be accomplished by UV irradiation of appropriate amine containing prepolymers in the presence of aromatic ketones and vinyl monomers. Previously, we have prepared amino functional polystyrene by following functional azo-initiator approach and subsequently used in photoinduced polymerization of methyl methacrylate (MMA) in the presence of 9-fluoronenone [6]. Semipinacol type radicals produced by the reduction of aromatic ketones are not noticeably active in initiation of polymerization of MMA at room temperature as observed by Ledwith [7]. This behaviour reduces homopolymer formation in the block copolymerization via photoreduction of aromatic carbonyls.



The amino functional polymers are not prepared only by free radical systems, but also by ionic routes. For example, a block copolymer composed of crystalline polyethylene oxide and non-crystalline polystyrene was prepared by combination of anionic polymerization and photoinduced H-abstraction polymerization [8]. More recently, this process was further extended to stable radical mediated radical polymerization. Wang et al. [9] prepared dimethylamino functional poly(ethylene oxide) macroinitiators by ring-opening polymerization of ethylene oxide using potassium 2-dimethylaminoethoxide. Subsequently, macroradicals generated by the photolysis of the amino terminal polymers in the presence of benzophenone were scavenged by 4-hydroxy-2,2,6,6-tetramethylpiperinyloxy (HTEMPO). Initiation of polymerization of St by HTEMPO terminated PEO by a living radical mechanism led to the formation of block copolymers.

Recently, there has been increasing interest in hyperbranched polymers, because they have a special structure, large number of terminal groups and physical properties differ from linear analogos, such as high solubility and low viscosity [10–13]. Hyper branched polymers can be prepared by the conventional polycondensation [14] reactions of AB2 type monomers and also by the use of so-called inimers. Inimers combine the features of both an initiator and a monomer [15–19]. Previously, the concept has been utilized in cationic polymerization [11], ring opening polymerization [20], controlled [21–23] and conventional radical [16,17] polymerizations and group transfer polymerization [24,25].

In this study, we report the synthesis of macroinimers of polyethylene oxide (PEO-macroinimer) possessing both polymerizable and radical generating sites, and the possibility of using these molecules in conjunction with benzophenone for the preparation of hyper branched networks via photoinduced hydrogen abstraction process.

2. Experimental

2.1. Materials

Ethylene oxide (EO) was purified by distillation over KOH, CaH_2, and finally over sodium mirror in vacuum. Benzophenone was recrystallized from ethanol. Methacryloyl chloride (MAC) and triethylamine were distilled under vacuum over CaH_2. Dimethylaminoethanol was dried and distilled under vacuum (10^{-5} Torr). Potassium naphthalene was prepared under vacuum from naphthalene (purified by sublimation) and potassium (distilled from melt) and dissolved in THF. The concentration was 0.46 $mol\,l^{-1}$ (titrated by potassium biphthalate for an aliquot). THF was purified and distilled over disodium salt of (α-methylstyrene) tetramer. All reagents or solutions were sealed into appropriately calibrated ampoules with a breakable seal under vacuum.

2.2. Preparation of PEO macroinimer

Calibrated amounts of dimethylaminoethanol (1 ml, 10 mmol), potassium naphthalene (0.46 $mol\,l^{-1}$, 14 ml) in THF, THF (total 115 ml), and EO (10 ml, 200 mmol), each in a ampoule with a breakable seal, were fitted into a flask, baked under vacuum, and sealed off from the vacuum line. Dimethylaminoalcohol and THF were first introduced into the cleanly dried flask and then reacted with potassium naphthalene in THF. The dark green color due to potassium naphthalene almost immediately disappeared. Then, EO, chilled by dry ice/isopropanol, was introduced to the flask, and polymerized at 40 °C over 3 days. The flask was then fitted into a vacuum line with calibrated ampoules containing MAC (3 ml, 30 mmol) and triethylamine (1 ml, 10 mmol). After evacuation, the system was sealed off, and the contents were

mixed to react by breaking the breakable seals. The reaction took place immediately with a cloudy appearance indicating formation of KCl and Et_3NHCl. The polymer yield was almost quantitative.

2.3. Photopolymerizations

The course of the polymerization was followed by ^{1}H-NMR measurements. Appropriate solutions of PEO macroinimer and benzophenone mixed in NMR tubes in $CDCl_3$ and degassed with nitrogen prior to irradiation by a super high pressure mercury lamp, Wacom HX-500, Type BMO-5000D1, Wacom R&D Corp., Japan, emitting light nominally at $\lambda = 350$–365 and equipped with a cooling system. At given intervals conversions were calculated from the ratio of the integration of the olefinic protons to that of the internal standard TMS. For the homopolymerization and copolymerizations, a similar procedure was followed except that the mixtures were contained in pyrex tubes in dry dichloromethane and precipitated in hexane at the end of irradiation. Soluble and insoluble fractions were separated by extraction with benzene. For the solid state photopolymerizations, films were prepared by solvent casting. Dichloromethane solutions containing 50 wt.% PEO-macroinimer and 2 wt.% benzophenone were poured onto glass plates and left overnight under a nitrogen stream followed by drying in a vacuum oven. Transparent films were irradiated for 4 h. The percentage of crosslinking was determined gravimetrically by extracting with benzene.

2.4. Swelling studies

Films of crosslinked polymers with a thickness of about 0.8–1 mm were cut into 1×1 cm pieces. Samples were then immersed in pure benzene, dichloromethane or water at room temperature until equilibrium swelling was reached. Then samples were taken out and the excess solution deposited on the film surface was removed quickly with blotting paper, and samples were weighed. The swelling degree was calculated by the equation:

$$\text{swelling } (\%) = (W - W_0)\ 100/W_0$$

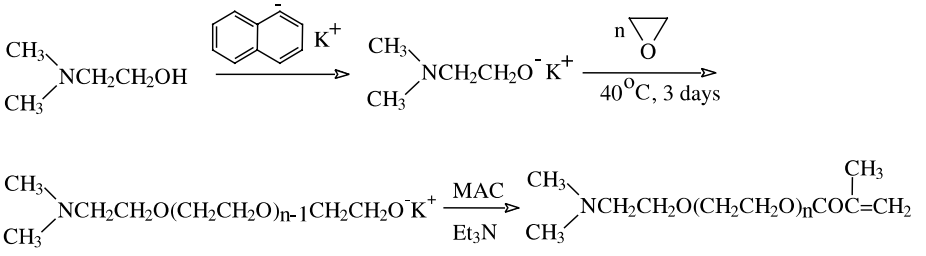
where W and W_0 are the swollen and dry samples, respectively.

2.5. Analysis

^{1}H-NMR spectra were recorded on a Varian Mercury 300 spectrometer in $CDCl_3$ at 20 °C. Size exclusion chromatography (SEC) for the characterization of macroinimer was run at 40 °C with JASCO PU980 as a pump, JASCO RI-930 as a refractive index detector, and Shodex A-802 and A-803 as columns. The signals were recorded on a computer and analyzed with a a SIC 480 data station software (Ver. 2.1A, SIC Inc., Japan). THF was used as an eluent at a flow rate of 1 ml min^{-1}. The elution volume was calibrated with standard samples of PEO from Tosoh Co., Ltd.

3. Results and discussion

Both styrene and methacrylate functionalities can be readily introduced to the chain ends of polyethylene oxide by utilizing appropriate initiation and end capping reactions [26,27]. In this study, we have chosen to introduce methacryloyl functionality as the polymerizable group since styrenic molecules are known to quench photoexcited benzophenone [28]. Moreover, α-aminoalkyl radicals are relatively less reactive towards styrene [29]. Thus, poly(ethylene oxide) macroinimer (PEO macroinimer) with methacryloyl functionality was prepared by anionic polymerization of ethylene oxide with amino functional initiator and termination of the living ends with methacryloyl chloride (MAC) according to the following reactions:



PEO-macroinimers were characterized by ^{1}H-NMR and GPC. Fig. 1 shows the ^{1}H-NMR spectrum of a typical macroinimer (Table 1, Run 1). Proton signals appearing at 2.8 ppm (N–CH_3), and 5.6 and 6.2 ppm (C=CH_2), proved the success of the initiation and termination reactions. The relative efficiency of functionalization for

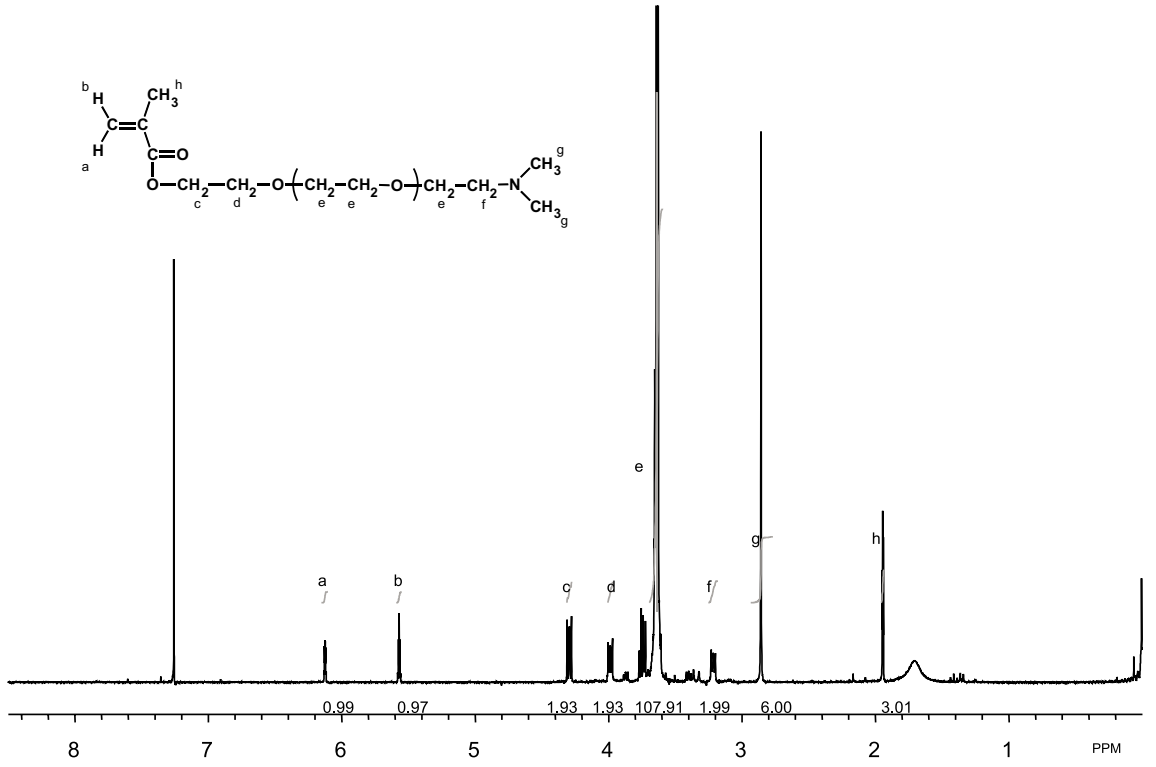


Fig. 1. ^{1}H-NMR spectrum of PEO-macronimer (Table 1, Run 1) in $CDCl_3$.

methacrylate groups could also be calculated from NMR data by using the peak area ratio of amino methyl and *cis* or *trans* protons of the double bond to versus the methylene protons at 3.6 ppm and assuming amino functionality is equal to 1.

Table 1 gives data for the characterization of macroinimers. As can be seen from Table 1, according to NMR results the amino functionality is equal to the acrylate functionality. Thus, a perfect functionality of 1 is produced for both amino and acrylate groups. However, there is some discrepancy between the M_n values measured by GPC and calculated by NMR. GPC data relies on calibration and thus less trustworthy.

Photoinduced polymerization of the macroinimer was expected to occur via hydrogen abstraction by the benzophenone triplet from the amino end group of the macronimer according to the following reactions.

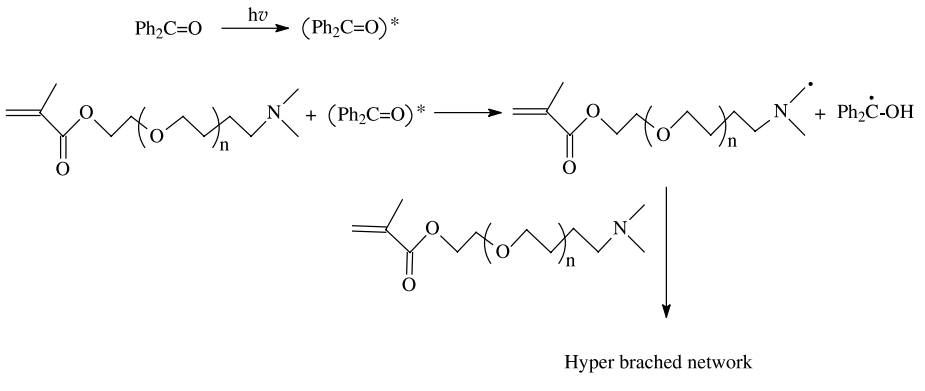


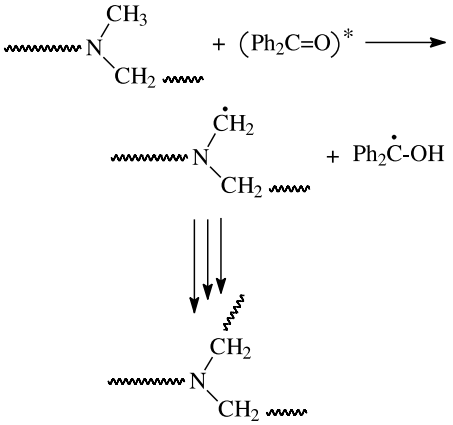
Table 1
Data for preparation of PEO-macroinimers

Run	$M_{n,kin}$ [a]	M_n, NMR [b]	$M_{n,GPC}$ [c]	M_w/M_n, GPC [c]	$f_{methacrylate}$ [b]
1	1038	1364	815	1.13	0.99
2	1220	1169	1042	1.07	1.08
3	2181	2190	2290	1.14	0.99

[a] Calculated kinetically by $M_{n,GPC} = 44[EO]_0/[\text{dimethylaminoethanol}]_0 + 157$, assuming living polymerization with quantitative conversion of EO and $f_{amino} = f_{methacrylate} = 1$.
[b] Determined by ^{1}H-NMR, assuming $f_{amino} = 1.0$.
[c] Determined by GPC.

The conversions were estimated by NMR spectroscopy using the integration ratio of olefinic protons at 6.2 and 5.6 ppm to TMS standard signals (Fig. 2). The conversion increased as the irradiation time increased (Fig. 3).

As can be seen from Table 2, homo and copolymerization of the macroinimer with MMA resulted in the formation of crosslinked polymers. Similar behaviour was also observed by Hazer [17] who utilized azo type macroinimers. In our case, although at a lower rate, the possibility of further H-abstraction from the second methyl group incorporated to nitrogen atom is an additional reason for the crosslinking reactions.



Further studies for obtaining linear hyper branched polymers by capping photochemically generated radicals with a stable radical such as 2,2,6,6-tetramethylpiperinyloxy (TEMPO) radical and subsequent stable radical mediated polymerization are currently in progress.

For the potential use of the system in water-borne photoresist applications, we have also tested photocuring in the solid state. Thus, irradiation of PEO-macroinimer film containing 1.33% (w/w) benzophenone for 4 h resulted in almost complete crosslinking (>95%). The crosslinked polymer exhibited interesting swelling behaviour. As can be seen from Table 3, the swelling value in dichloromethane and water is extremely high indicating hyper-branched nature of the photocrosslinked macroinimer.

It is also interesting to note that excess solvent uptake in the case of water caused some physical split of the network. Relatively low swelling value in the case of

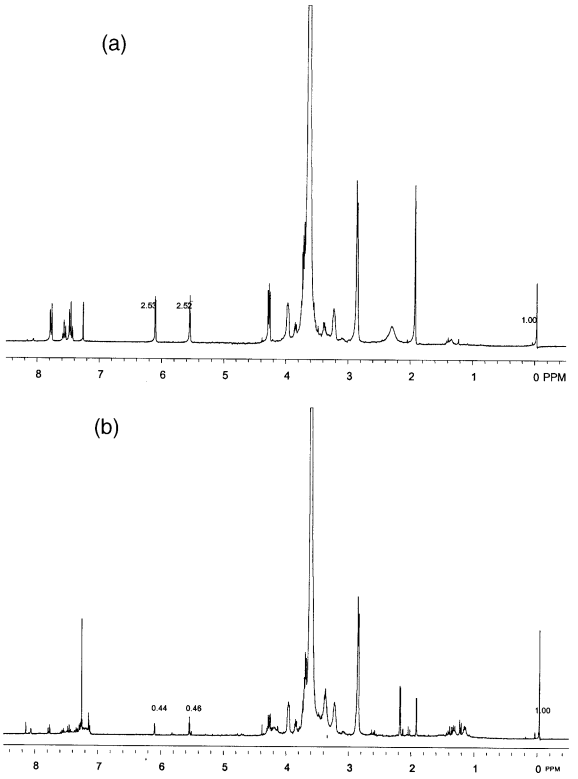


Fig. 2. ^{1}H-NMR spectra of the polymerization mixture in $CDCl_3$ before (a) and (b) after 70 min irradiation. [PEO-macroinimer, (Table 1, Run 1)] = 1.2×10^{-1} moll^{-1}, [Benzophenone] = 2.7×10^{-2} moll^{-1}. The numbers at the resonance lines represents the integration ratios of the signals.

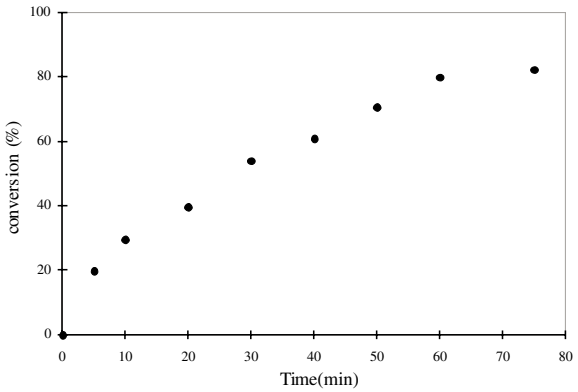


Fig. 3. Time–conversion plot for the polymerization of PEO-macroinimer in $CDCl_3$.

Table 2
Photoinduced polymerization and copolymerization of PEO-macroinimer (Table 1, Run 1) with methyl methacrylate in dichloromethane at room temperature

Run	[Macroinimer] ($mol l^{-1}$)	[MMA] ($mol l^{-1}$)	[Benzophenone] ($mol l^{-1}$)	Irradiation time (min)	Conversion (%)	Crosslink (%)
4	0.12	–	0.017	200	>99	<1
5	0.74	–	0.023	240	>99	91.7
6	0.74	2.3	0.023	240	97	56.6
7	0.74	3.8	0.023	240	48.4	70.9

Table 3
Swelling values of hyperbranched crosslinked macroinimer

Solvent	Swelling[a] (%)
Benzene	101
Dichloromethane	986
Water	1651

[a] $W - W_0/W_0 \times 100$.

benzene is expected due to the aromatic nature of the solvent.

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