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Macromolecular Architecture Based on Anionically Prepared Poly(ethylene oxide) Macromonomers

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Summary: Synthesis of poly(ethylene oxide) (PEO) macromonomers carrying a methacyloyl group in one end, and *N, N*-dimethyl amino, thiophene, styryl and vinyl ether functional groups in the other end was desribed. The general synthetic strategy is based on the living anionic polymerization of ethylene oxide initiated with functional potassium alcoholates, followed by reaction with methacyloyl chloride. These macromonomers were further utilized in various macromolecular architectures through via concurrent or selective thermal free radical, oxidative and photoinitiated free radical and cationic polymerization methods. The use of this synthetic route to prepare graft copolymers possessing completly and perfectly alternating PEO side chains using charge-transfer-complex polymerization was also demonstrated.

Keywords: cationic polymerization; electropolymerization; free radical polymerization; macromonomer; photopolymerization, poly(ethylene oxide)

Introduction

Design and synthesis of materials with novel properties is becoming an increasingly important aspect of polymer chemistry. In this regard, telechelics and macromonomers have been known as useful building blocks for such materials[1]. In general, however, the functional end-groups introduced have been of the same structure because of simplicity in synthesis. Different functionalities have to be usually introduced by some complicated procedure such as protection/deprotection, as in the case of PEO-based macromonomers with an ω-functional group such as a hydroxyl [2] or an aldehyde [3,4]. Soula and Guyot used potassium *p*-vinylbenzylate to sequentially polymerize 1,2-epoxybutane and ethylene oxide (EO), followed by reaction with propane sultone to prepare α-*p*-vinylbenzyl-ω-sulfonyl-PEO macromonomers [5] In this paper, we report a simple method to prepare such hetero-functional PEO macromonomers by taking advantage of the living anionic polymerization of EO [6-9].

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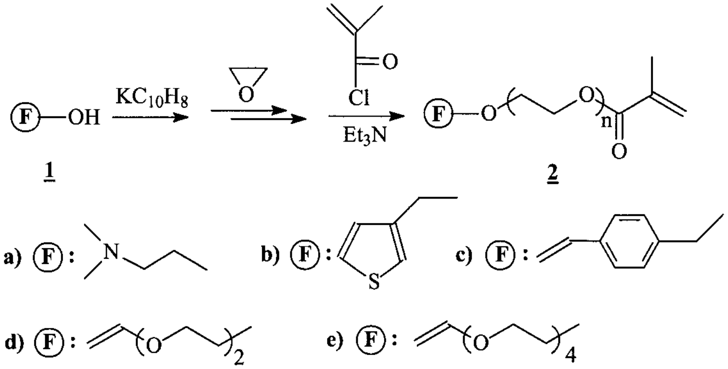
Synthetic Strategy for the Preparation of Hetero-functional PEO Macromonomers

As depicted in Scheme 1, various heterofunctional macromonomers were prepared by utilizing both functional initiator and terminator approaches successively in the ring opening anionic polymerization of ethylene oxide. We start with a functional alcohol, F-OH, and add potassium naphthalene ($KC_{10}H_8$), to initiate the EO polymerization to readily afford the mono-functional poly(ethylene glycol), F-O-$[CH_2CH_2O]_n$. The living end group can then be transformed into appropriate functionalities, F', to give α,ω-hetero-telechelic PEOs, F-O-$[CH_2CH_2O]_n$-F'. In this manner we have prepared α-*p*-vinylphenylalkyl-ω-hydroxy-, [6] α-dimethylamino-ω-methacryloyl-, [7] α-*p*-vinylbenzyl-ω-dimethylaminoethyl-, [8] and α-3-thienylethyl-ω-methacryloyl-terminated PEO macromonomers [9].



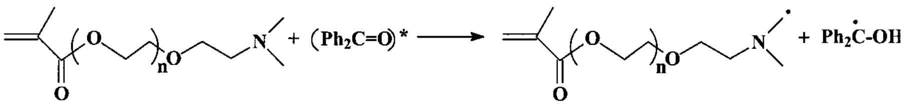
Scheme 1. Synthesis of hetero-functional macromonomers.

Photoinitiated Free Radical Polymerization PEO Macroinimers: Hyrdogels Based on PEO

Hydrogels derived from PEO are useful in biomedical and pharmaceutical applications because of their biocompatibility and high water contents. We have recently demonstrated[9] that PEO-macroinimer (***macro***molecule-***ini***tiator-mono***mer***), **2a**, possessing both polymerizable and radical generation sites was used to obtain hydrogels having dangling PEO chains. It was shown that the PEO-macroinimer acts during the photopolymerization, both as a monomer and a crosslinker and thus, leads to the formation of hydrogels of various swelling capacities and moduli of elasticity[10].

Hydrogen abstraction from one of the methyl groups adjacent to the amino group by a photoexcited benzophenone molecule[11, 12] leads to the formation of macroinimer and ketyl radicals, where the latter radical is known to undergo radical coupling and is thus, ineffective in initiating the polymerization reactions (Scheme 2).

$$Ph_2C{=}O \xrightarrow{h\nu} (Ph_2C{=}O)^*$$



Scheme 2. Photoinduced generation of radicals from PEO macroinimer in the presence of benzophenone.

In this connection, it should be pointed out that photoexcited benzophenone can also abstract hydrogen from PEO itself without the requirement of additional hydrogen donors[13, 14]. Thus, a portions of the initially difunctional macroinimer becomes trifunctional as a result of the hydrogen abstraction reaction from either terminal amino groups or PEO backbone, which seems to be responsible for the formation of an infinite network in the reaction system.

Free Radical and Oxidative Polymerization of the Hetero-functional Macromonomer

The hetero-functional macromonomer, **2b**, possesses thiophene and methacrylate functionalities. The ^{1}H-NMR spectrum of this macromonomer exhibits signals in the range of 7.31-6.92 corresponding to –CH protons of thiophene rings, 6.08-5.53 corresponding to vinyl protons, 4.27-4.23 ($COOCH_2$), 3.65-3.30 (CH_2O), 2.90-2.85(Thi-CH_2) and 1.92 ppm (CH_3) (Figure 1a).

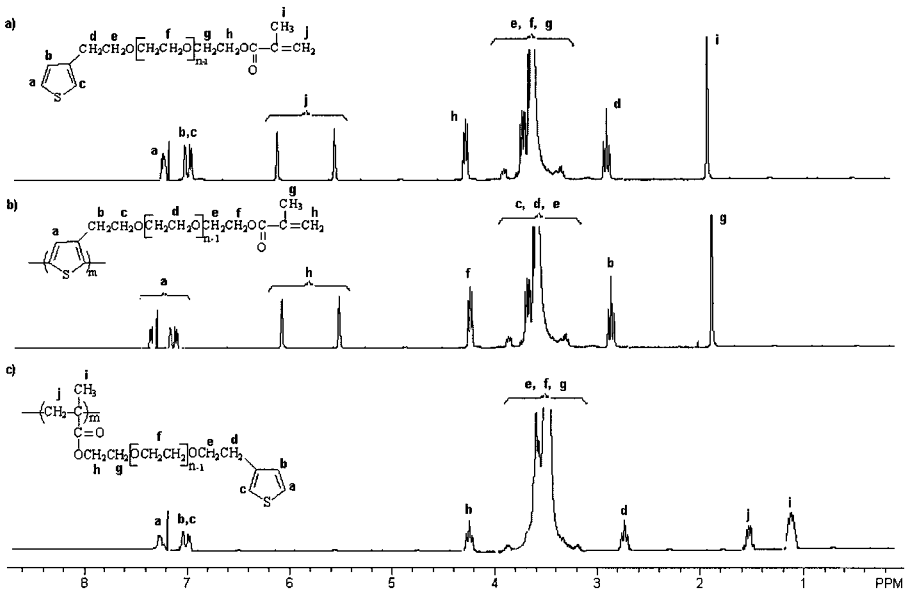
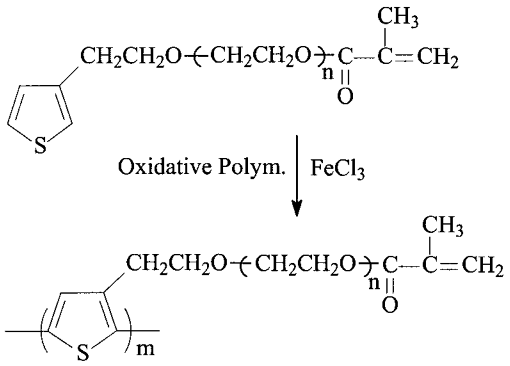


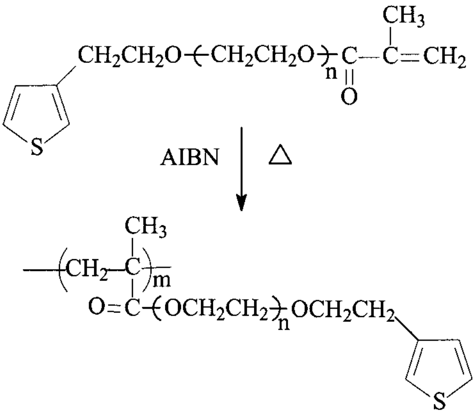
Figure 1. ^{1}H-NMR spectra of PEO Macromonomer, **2b** (a); after oxidative polymerization (b); after free radical polymerization (c).

The macromonomer **2b** was shown to polymerize selectively by oxidative and radical mechanisms through the thienyl and methacryloyl end-groups, respectively[9]. The macromonomer, having an electroactive group, was first polymerized oxidatively in the presence of $FeCl_3$ as an oxidant (Scheme 3). The structure of the soluble part of graft copolymer was characterized by ^{1}H-NMR. The decrease in the ratio of the integral peak area of the signals at 7.31-6.92 ppm corresponding to –CH protons of thiophene rings to that of ethylene oxide can be attributed to the fact that polymerization took place, most probably, at the 2 and 5 positions of the thiophene rings (Figure 1b). Also, the vinylic double bond was not affected during the chemical polymerization



Scheme 3. Oxidative polymerization of the hetero-functional macromonomer, <u>2b</u>.

The macromonomer was also used in homopolymerization via the vinylic terminus. The reaction involves the free radical polymerization of PEO macromonomer in the presence AIBN as a thermal initiator. Scheme 4 indicates the reaction path. The structure of homopolymer was characterized by ^{1}H-NMR spectroscopy and GPC measurements. The disappearence of the signals at 5.7-6.1 ppm corresponding to vinylic protons and the apperance of the signal at 1.47 ppm corresponding to $-CH_2C(CH_3CO$-) shows that the homopolymerization of macromonomer proceeded via the vinylic bond (Figure 1c).



Scheme 4. Free radical polymerization of the hetero-functional macromonomer, <u>2b</u>.

Photoinitiated Cationic and Free Radical polymerization of Hetero-functional Macromonomers

More recently, we have described[15] novel hybrid PEO macromonomers carrying conventional but different vinyl end-groups which can polymerize in different ways by a radical, cationic, and/or anionic mechanism. Therefore, the preparation of hybrid PEO macromonomer, **2c**, with a styryl at one end and methacryloyl group on the other end has been readily accomplished by polymerization of EO with *p*-vinylbenzyl alcohol (VBA), **1c**, partially alkoxidated with $KC_{10}H_8$, followed by reaction with methacryloyl chloride (MAC), as shown in Scheme 1 . The presence of both styryl and methacryloyl end groups in nearly 1 : 1 ratio was confirmed by NMR spectral analysis. The molecular weight estimated from the integration of oxyethylene protons relative to that of methacryloyl methylene protons is in fairly good accord with the value expected from the ratio of EO to VBA in the feed and also with that determined by GPC calibrated with standard poly(ethylene glycol)s, as in Table 1. The molecular weight distribution is also fairly narrow. We can expect even easier preparation of vinyl ether-ended PEO methacrylate macromonomers because the vinyl ethers are much less easily attacked by $KC_{10}H_8$ or by oxy anions. Thus both di(ethylene glycol) monovinylether (DEVB), **1d**, and tetramethylene glycol monovinylether (TMGV), **1e**, (Scheme 1) satisfactorily afforded the corresponding macromonomers, **2d** and **2e** as is clear in Table 1.

Table 1. Molecular weight characterization of the hetero-functional PEO macromonomers.

Macromonomer	$10^{-2}\,M_{n,th}$ a)	$10^{-2}\,M_{n,NMR}$ b)	$10^{-2}\,M_{n,SEC}$ c)	M_w/M_n c)
2c	24	29	31	1.06
2d	12	13	16	1.03
2e	10	18	17	1.04

a) Theoretical value calculated by: $M_n = 44\,n + M_{F\text{-}O} + M_{MA}$, where n = [EO]/[F-OH] is the mole ratio of EO and the alcohol in feed, while 44, $M_{F\text{-}O}$, and M_{MA} are molecular weights of EO, the alcohol- and methacryloyl fragments, respectively.

b) Estimated by the same eq as above[a] with n by ^{1}H-NMR, i. e., from the integrated ratio of oxyethylene protons to methacryloyl protons.

c) Determined by GPC calibrated with standard poly(ethylene glycol)s.

Such hybrid macromonomers will be potentially attractive in controlled syntheses of network or gelled polymer materials with soft and hydrophilic domains or surfaces. One particularly interesting aspect of the use of these macromonomers deals with photopolymerization. Their reactivity in photoinitiated free radical and cationic systems was also studied[15] . The reactivity of the radical and cationic species formed upon photolysis of benzophenone and triphenylsulfonium tetrafluoroborate towards these end grous were studied by means of ^{1}H-NMR analysis following the disappearance of the respective olefinic groups (Figures 2 and 3).

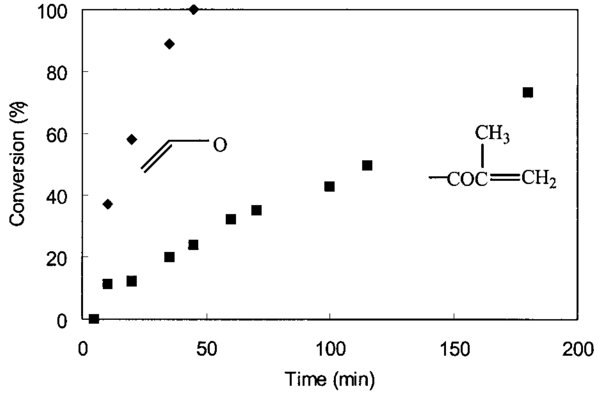


Figure 2. Disappearance of the double bonds of the hetero-functional macromonomer, 2d, during photolysis in the presence of benzophenone.

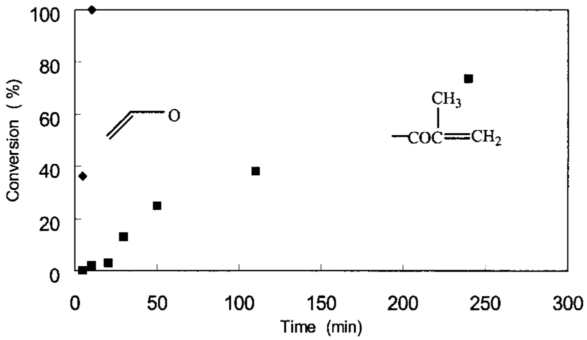


Figure 3. Disappearance of the double bonds of the hetero-functional macromonomer, 2d, during photolysis in the presence of triphenylsulfonium tetrafluoroborate.

As indicated before, the photoinitiating activity of benzophenone is promoted by hydogen donors. Regarding the photolysis mechanism of triarylsulphonium salts, both heterolytic and homolytic bond rupture of one sulfur-carbon bond is evidenced. In secondary reactions a strong electrophilic Brønsted acid is produced[16]. This acid initiates the cationic polymerization. The radical cations formed according to Scheme 5 can also react with the reactive monomers. For example, the bimolecular rate constant for the reaction of these radical cations with butyl vinyl ether was found to be 3.2 x 10^5 l $mol^{-1}s^{-1}$.[17]

$$Ph_3S^+X^- \xrightarrow{h\nu} Ph_2\overset{+\bullet}{S}X^- + Ph\bullet$$

$$Ph_2\overset{+\bullet}{S}X^- + R{-}H \longrightarrow Ph_2S + H^+X^- + R\bullet$$

Scheme 5. Photolysis of sulphonium salts.

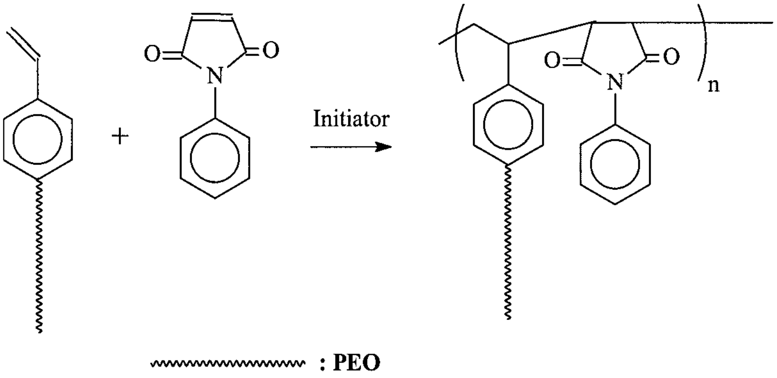
Studies with macromomonomers and model compounds revealed that photoexcited benzophenone abstracts hydrogen atoms from the PEO backbone to form radicals without added hydrogen donors. In the case of the sulfonium salt, both radicalic and cationic species are formed which react with the respective functional groups. It was also shown that vinyl ether moieties react more readily than the methacrylate in both radicalic and cationic processes. The rate for the disappearance of the vinyl ether double bond is about 50 times higher than that of the corresponding methacrylate bonds in the cationic mode (Table 2). It is interesting to note the influence of the spacer group between vinyl ether group and PEO chain. When the vinyl ether group is directly attached to PEO, **2d**, the reactivity is higher with the sulfonium salt. This behavor may be atributed to stronger electron donating effect of CH_2CH_2O than the $(CH_2)_4$ spacer group. Notably, the consumption of the methacrylate bond is faster with the free radical initiator, benzophenone with that of the sulfonium salt. As would be expected, photolysis in the presence of the sulphonium salt yielded almost complete conversion of the double bonds of the vinyl ether while the methacrylate bonds are only slightly effected.

Table 2. Rate of disappearance of the double bonds of various hetero-functional macromonomers with benzophenone and $Ph_3S^+BF_4^-$.

Macromonomer	Photoinitiator	$R_{dis.(\mathrm{VE})} \times 10^5$ (Mol l^{-1} s^{-1})	$R_{dis.(\mathrm{MA})} \times 10^5$ (Mol l^{-1} s^{-1})
2d	Benzophenone	1.06	0.28
2d	$Ph_3S^+BF_4^-$	4.8	0.16
2e	Benzophenone	3.3	0.54
2e	$Ph_3S^+BF_4^-$	2.7	0.17

Completely and Perfectly Alternating PEO Graft Copolymers

Maleimide monomers are known to form alternating copolymers with electron rich monomers[18]. Completly and perfectly alternating copolymers were obtained through the formation of a charge transfer complex (CTC) between styrene functional PEO macromonomer as electron-rich monomer and N-phenyl maleimide (NPMI) as electron-defficient monomer (Scheme 6).



Scheme 6. Charge transfer complex polymerization of styrene functional PEO macromonomer with *N*-phenyl maleimide.

Homogenous copolymerizations were performed[19] by using THF and benzene as solvents and in the mixture of water with THF or in water when dispersion polymerization or micellar copolymerization take place, respectively. While the NMPI feed mole content varies over a large range, the mole ratio of the comonomers incorporated in copolymers was found to be close to 1. This fact confirms the formation of a CTC between the macromonomer and NMPI, and its participation in both initiation and propagation steps of the copolymerization. This concept may be of considerable importance for the preperation of well-defined amphiphilic copolymers containing perfectly and completly alternating hydrophilic and hydrophobic side chains. Further studies in this line by using maleimide macromonomers of hydrophobic polymers in conjunction with styrene functional PEO macromonomers are now in progress.

Acknowledgement

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