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A REVIEW OF POLY(ETHYLENE OXIDE)-BASED BLOCK COPOLYMERS

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ABSTRACT

The block copolymers synthesized via redox, thermal free radical, photo induced ionic and step growth polymerization using the macro initiators containing poly(ethylene oxide) segments are reviewed.

INTRODUCTION

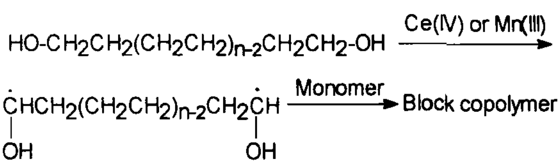
Poly(ethylene oxide)(PEO) and their derivatives have a widespread usage in chemical, biomedical and industrial applications resulting from their low cost, non-toxic and useful properties such as solubility in water and common organic solvents, metal complexing ability, biological compatibility and ease of chemical modification[1-2]. Such applications include peptide synthesis, phase transfer catalysis, polymer bound reagent and binding assays. The synthesis of PEO derivatives are reviewed by Harris and coworkers[1-3].

PEO and its derivatives were also used as a macro initiator in block and graft copolymer synthesis via different polymerization methods. PEO-Macro initiators used in the synthesis of graft copolymers named macromonomers were reviewed by Ito[4].

The present review article refers to the synthesis of block copolymers starting from PEO-macroinitiators.

1. BLOCK COPOLYMERS CONTAINING PEO PREPARED BY REDOX POLYMERIZATION

Polymerization of a vinyl monomer by a redox system consisting of transition metal ions such as Ce(IV), Mn(III) and poly(ethylene glycol)(PEG) may be represented as follows:



Different block and multiblock copolymers prepared by PEG-redox macroinitiators are tabulated in the following Table 1.

Table 1. Block copolymers containing PEO prepared by PEG-redox macroinitiators

Block copolymer	Redox system	References
Poly(acrylonitrile-b-ethylene oxide)n	PEG/Ce(IV)	5, 6
	PEG/Mn(III)	7
	PEG-Xanthate/H_2O_2	8, 9
Poly(methyl methacrylate-b-ethylene oxide-b-methyl methacrylate)	PEG/Ce(IV)	10, 11
	Deodecyl-PEG/Ce(IV)	12
	PEG-Xanthate/H_2O_2	13
	PEG/Mn(III)	14
Poly(acrylamide-b-ethylene oxide-b-acrylamide)	PEG/Mn(III)	14
	PEG-b-PAAm/Ce(IV)	15
Poly(methyl methacrylate-b-ethylene oxide-b-styrene-ethylene oxide-b-methyl methacrylate)	PEG-azoester/Ce(IV)	16(a)
	PEG-azoester/Mn(III	16(b)
Poly(acrylamide-b-ethylene oxide-b-acrylonitrile-ethylene oxide-b-acrylamide)	PEG-azoester/Ce(IV)	17

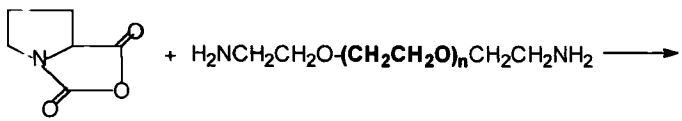
2. PEO-BLOCK COPOLYMERS SYNTHESIZED VIA IONIC OR RING OPENING POLYMERIZATIONS

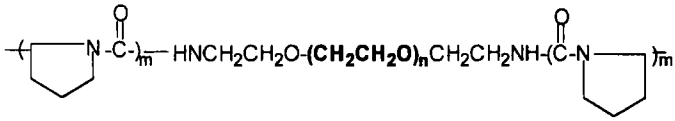
Suzuki et. al[18-20] reported the anionic polymerization of methyl methacrylate initiated with the sodium salt of PEO in THF in both the presence and absence of a crown ether cryptate in this work, a linear triblock copolymer of PMMA-PEO-PMMA having unimodal a narrower molecular weight distribution.

1,3,5-Trioxane and 1,3 dioxalane were polymerized in the melt in the presence of different PEG using BF_3.ethereate as catalyst[21].Thereby the polyether are incorporated as block via a chain transfer reaction with their terminal hydroxyl groups.

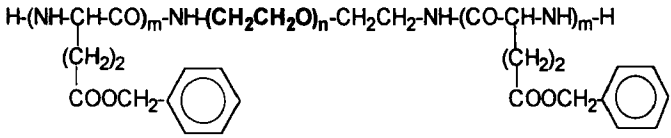
ABA-Type block copolymers composed of poly(γ-benzyl-L-glutamate) as A component and poly(ethylene oxide) as the B component were synthesized by the anionic polymerization of γ-benzyl L-glutamate N-carboxyanhydride initiated with primary amines located at both ends of the PEO chain[22].

A water soluble ABA type block copolymer of poly(l-proline) and poly(ethylene oxide) was prepared by the anionic polymerization of L-proline N-carboxy anhydride using an amino terminated PEO macroinitiator[23].





A similar method[24] was also used to obtain poly(γ-benzyl-L-carboxy-L-glutamate-b-ethylene oxide) block copolymer having the following structure:



Styrene-ethylene oxide star block copolymers were prepared by treating living PS with living PEO in the presence of $SiCl_4$ or $MeSiCl_3$ coupling reagents [25].

Reuter at. al.[26] have reported the synthesis of t-butyl methacrylate-ethylene oxide block copolymers by anionic polymerization using a monofunctional initiator in THF.

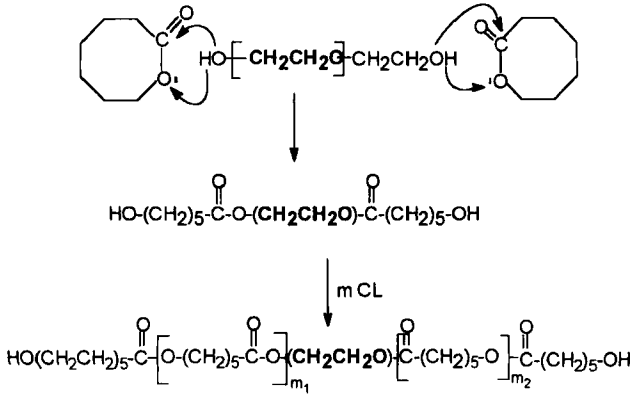
Alkali metal salts of poly(ethylene glycol)s and poly(ethylene glycol) mono methyl ethers were used as initiators for the anionic ring opening polymerization of 2,2-dimethyl-trimethylene carbonate to yield ABA and AB type block copolymers[27].

ABA-type block copolymers composed of poly(ε-benzoyloxycarbonyl-L-lysine) as the A component and poly(ethylene oxide) as the B component were synthesized by polymerization of ε-benzoyloxycarbonyl-L-lysine N-carboxy anhydride initiated by primary amino groups located at both end of PEO chain[28].

The poly(ethylene oxide)/poly(L-lactide) copolymers were prepared copolymerization of L-lactide a PEG with number-average molecular weights Mn for 1000 to 600[29].

Hashimoto et al[30] synthesized the block copolymers composed of polyamide as the outer segment and poly(oxyethylene) as inner segment by the anionic ring polymerization of a bicyclic oxalactam, 8-oxa-6-aza bicyclo[3.2.1] octan-7-one, activated with poly(oxyethylene) of different molecular weight having isocyanate groups at both chain ends. The block copolymer structure represented as follows:

Andruzzi et. al.[31] were prepared poly(ethylene glycol-b-ε-caprolactone) via polymerization of ε-caprolactone with PEG of low molecular mass in bulk at 185 °C. Reaction pathways represented as follows:



To obtain poly(ethylene oxide-b-β-propiolactone) block copolymers, similar method was also used by Andruzzi et. al.[32].

Perret and Skoulios[33] were polymerized ε-caprolactone via anionic ring opening polymerization using the sodium salt of PEO prepared with Na-naphtlane in benzene to yield poly(ethylene oxide)-poly(caprolactone) block copolymers.

Block copolymer composed poly(N-acylethyleneimine) and poly (oxyethylene) segments were prepared by initiating cationic ring opening polymerization of 2-methyl oxazoline and 2-ethyl oxazoline with ditosylated poly(ethylene oxide)[34].

Poly(butadiene-b-ethylene oxide-b-methyl methacrylate)[35], poly (butadiene-b-ethylene oxide-b-styrene), [34] poly(butadiene-b-ethylene oxide)[36-37] and poly(ethylene oxide-b-butadiene-b-styrene-butadiene-b-ethylene oxide)[38] block copolymers were prepared via sequential living anionic polymerization.

The synthesis of poly(methyl methacrylate-b-ethylene oxide-b-methyl methacrylate) triblock copolymers via anionic polymerization have been reported by Tomoi et al.[39].

A series of AB-type diblock copolymers composed of poly(styrene) as the A block and poly(ethylene oxide) as the B block was synthesized by sequential anionic initiation using cumyl ether as catalyst[40].

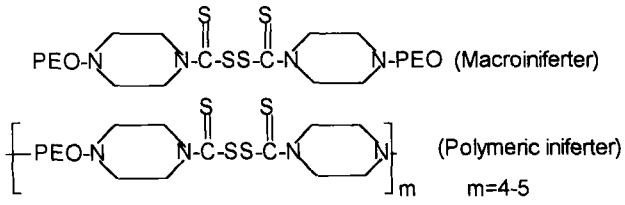
PS-PEO block copolymers were also synthesized by several investigators via sequential anionic polymerization using different catalysts[41-57].

Lyman et. all.[58] have reported the synthesis of a five block copolymer of the type ABCBA, wherein A was PEO and B and C could be either polystyrene or polyisoprene using potassium naphthalide as anionic initiator via sequential anionic living polymerization.

Block copolymer of D,L- Lactide and PEG with narrow molecular weight distribution were prepared in the presence of several cationic initiators[59].

3. Poly(ethylene oxide) Containing Block Copolymers Prepared by the Combinations of Free Radical and Condensation polymerization

Nair et. al.[60] have reported the synthesis of three and multiblock copolymers of styrene and ethylene oxide through PEO based thermal iniferters as shown below.



Thermal polymerization of styrene in the presence of macroiniferters lead to formation of their triblock copolymers, with styrene forming central block. When the polymeric iniferter used in the polymerization of styrene, (AB)n type multiblock copolymers were obtained.

A poly(ethylene oxide-b-hydroxyethyl celulose) block copolymer was prepared via ultrasonic degradation of hydroxyethyl cellulose in aqueous solution[61].

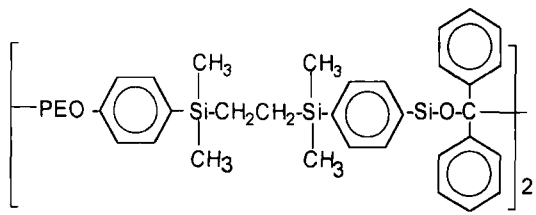
A block copolymer of MMA and PEO was synthesized by initiation with PEO radicals formed by high speed stirring[62].In this work, the effects of the concentration of the reagents, the rotation speed and the degree of polymerization on the rate of the block copolymerization was also investigated.

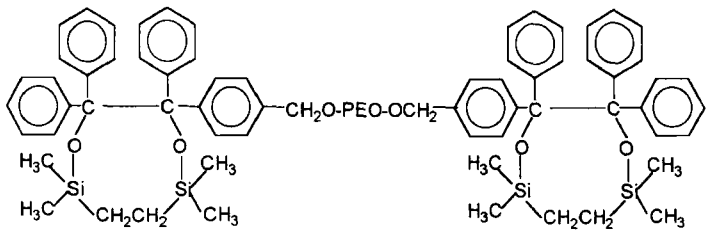
Segmented poly(ethylene oxide) macroinitiators containing bis alkyl benzopinacolate groups were used to initiate thermal radical polymerization of styrene[63]. A PS-PEO block

Table 2. Block copolymers prepared by macroazoinitiators possessing PEO chain.

Polymer A	Polymer B PEO	Reference
polyacrylate copolymer		64
poly(methyl methacrylate)		65-67
poly(styrene)		68-71
poly(vinyl acetate)		72
poly(vinyl chloride)		73-74
poly(styrene-b-methyl methacrylate)		75-76
Poly(vinyl acetate-co-acrylic acid)		73-74,77
Poly(acrylamide)		78
Poly(acrylamide-b-vinyl acetate)		78
Poly(acrylamide-b-ethyl acrylate)		78

copolymers were obtained by the incorporation of the PEO-macroinitiators having following structures:





Macroazoinitiators containing azo and poly(ethylene oxide) prepared 2,2'-azo-bis-(isobutyronitrile) or 4,4'-azo-bis-(4-cyanopentanoic acid) and PEG via Pinner reaction can be used to synthesize block copolymers by radical polymerization in one or two step procedure. Various block copolymers have been synthesized by macroazoinitiators having PEG segment. These are summarized in Table 2.

4. Block Copolymers Synthesized by Step Growth Polymerization

Table 3. PEO containing block copolymers obtained by step growth polymerization

Block copolymer	Reference
poly(ethylene oxide-b-3,3-dimethylthioethane)	79
poly(ethylene oxide-b-amido amin)	80
poly(ethylene oxide-b-amido amin-urethane)	81
poly(ethylene oxide-b-oxy-2-methyl-trimethylene)	82
poly(ethylene oxide-b-isopropylacrylamide)	83
poly(ethylene oxide-b-choloroformyl-ethyl)	78
poly(ε-caprolactam-b-ethylene oxide-b-ε-caprolactam)	84-85
poly(caprolactone-b-ethylene oxide-b-caprolactone)	86
poly(diphenyl methyl diisocyanate-b-ethylene oxide)	87
poly(thioether/amide acid-b-ethylene oxide)	88
poly(amido ether-bethylene oxide)	89
poly(ethylene terephtalate-b-ethylene oxide)	90
poly(ethylene oxide-b-β-benzyl L-aspartate)	91
poly(ethylene glycol-b-Bisphenol-A)	92-94
poly(m-phenylene isophtalimide-ethylene oxide)	95
poly(m-styrene-b-ethylene oxide-b-styrene)	96
poly(m-phenylene isophtalimide-b-ethylene oxide-b-dimethyl siloxane)	97
poly(dimethyl siloxane-b-(ethlene oxide-co-propylene oxide))	98
poly(ethylene oxide-b-adipoyl-ethylene oxide)	99
poly(ethylene oxide-b-propylene oxide)	100-101
poly(ethylene glycol-b-ethylene succinate)	102
poly(butadiene-b-ethylene oxide-b-butadiene)	103-104
poly(ethylene oxide-b-hexamethylene diamin)	105
poly(ethylene oxide-b-terephtalate)	106
poly(ethylene oxide-b-styrene)	107
poly(ethylene glycol-b-dimethyl siloxane)	108
poly(ethylene glycol-b-bisfenol-A)	109
poly(ethylene oxide-b-dimethyl siloxane)	110
poly(ethylene oxide-b-propylene oxide-b-octamethylcyclotetrasiloxanes)	111
poly(dimethyl siloxane-b-oxyethylene-b-oxypropylene)	112-113
poly(tetramethyl siloxane-b-ethylene oxide-propylene oxide)	114
poly[(oxyethylene-b-(adipic acid-co-1,3-bis(3-aminopropyl)-5,5-dimethyl thylhydantoinn)	115
poly(ethylene oxide-b-2-hdroxyethyl methacrylate)	116
poly(3,3-ioene chloride-b-ethylene oxide-b-3,3-ionene chloride)	117
poly(oxyethylene-b-oxypropylene-b-styrene)	118
poly(styrene-b-ethylene oxide-b-styrene)	119-120

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