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Molecular design, synthesis and properties of block and graft copolymers containing polyoxyethylene segments

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Abstract

This article deals with recent progress including the author's work concerning the molecular design, synthesis, purification, characterization and physical properties of seven types of multiphase copolymers of styrene (S) and ethylene oxide (EO), namely, PS–PEO diblock copolymers, PS–PEO–PS and PEO–PS–PEO triblock copolymers, star-shaped block copolymers, multiblock copolymers, PEO–g-PS, PS–g-PEO graft copolymers and five types of alkyl (meth)acrylate and ethylene oxide multiphase copolymers as well as other types of block and graft copolymers from ethylene oxide and diene or other vinyl (or acrylic) monomer. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Amphiphilic block and graft copolymers consisting of hydrophilic and hydrophobic parts have been subjects of numerous studies, within which block and graft copolymers containing hydrophilic polyoxyethylene segments and other hydrophobic segments have attracted much attention, because polyoxyethylene segments are not only hydrophilic, but also nonionic and crystalline, and can complex monovalent metallic cations. The amphiphilic nature of these copolymers containing incompatible segments gives rise to special properties in selective solvents, at surfaces as well as in the bulk, owing to microphase separation morphologies. They have many uses including polymeric surfactants, electrostatic charge reducers, compatibilizers in polymer blending, phase transfer catalysts or solid polymer electrolytes, etc.

This article deals with recent progress including our work concerning the molecular design, synthesis, purification, characterization and physical properties of seven types of multiphase copolymers of styrene (S) and ethylene oxide (EO), namely, PS–PEO diblock copolymers, PS–PEO–PS and PEO–PS–PEO triblock copolymers, star-shaped block copolymers, multiblock copolymers, PEO–g-PS, PS–g-PEO graft copolymers and five types of alkyl (meth)acrylate and ethylene oxide multiphase copolymers as well as other types of block and graft copolymers from ethylene oxide and diene or other vinyl (or acrylic) monomer.

2. Block copolymers from ethylene oxide and styrene

2.1. PS-PEO diblock copolymers

The PS–PEO block copolymer(AB type) was synthesized by O'Malley et al., via a sequential anionic polymerization of styrene and EO with cumylpotassium as initiator [1].

Quirk and Seung [2] prepared diblock copolymer, PEO–PS, in 83% yield by polymerization of EO at 40°C–60°C for 8 days in the presence of LiOCH₂CH₂-terminated PS in 2 : 1 C_6H_6 –DMSO (dimethyl-sulfoxide). A dipolar aprotic solvent such as DMSO provided the necessary solvation and polarity to render Li alkoxide an effective initiator for EO polymerization. Polymerization of EO with NaMg(C₄H₉)₃ gives 22% copolymer after 3 days at 60°C and 56% copolymer after 12 days at 60°C. Little or no polymerization of EO was observed in the presence of the polystyryllithium–C₆H₆–TMEDA (tetramethyl ethylene diamine) system.

Ueda and Nagal [3] synthesized block copolymers of styrene and EO through polycondensation between azobiscyanopentanoyl chloride and polyethylene glycol (PEG), followed by thermal decomposition in the presence of styrene (Scheme 1).



Yuruk and Ozdemir [4] prepared the block copolymer using polymeric azocarbamate as an initiator, which was obtained by capping polyethylene glycol with aliphatic diisocyanate and subsequently by reacting this intermediate with azobiscyanopentanol. The macroazocarbamate was then used to initiate the free radical polymerization of styrene at elevated temperature (Scheme 2).

Niwa et al. [5] synthesized a macroinitiator through reaction of sodium ω -methoxypoly(ethylene glycol) (MPEG) with tribromoacetyl chloride. Styrene was initiated with the macroinitiator in the presence of manganese carbonyl to form block copolymer (Scheme 3).

PS–PEO diblock copolymers were synthesized by Xie and Zhou [6] through sequential anionic polymerization of styrene and EO with α -phenyl ethyl potassium as an initator in toluene according to the following equation (Scheme 4):During the polymerization of styrene using this initiator, an induction period was observed, which decreased with increasing polymerization temperature. This induction period can be somewhat shortened by adding a certain amount of tetrahydrofuran corresponding to the molar equivalent of α -phenyl ethyl potassium. Probably the induction period is not because of association of catalyst, but owing to the increase of catalyst solubility in toluene with the increase of temperature, resulting in the change from heterogeneous phase to homogeneous phase and a shortening of the induction period. Increasing temperature for the copolymerization of living PS with EO from 10°C to 30°C enhanced the conversion of EO greatly. At 30°C, 92% conversion of EO was reached within 11 h.







Scheme 3.

Water and hot cyclohexane were proved effective as extracting agents for PEO and PS homopolymers, respectively. The diblock copolymer after purification by extraction appears white and granular, insoluble in cyclohexane, swelling in water, but soluble in benzene, toluene, tetrahydrofuran and acetone.

The IR spectrum of the purified diblock copolymer indicated a characteristic peak at 1120 cm⁻¹ for the ether linkage, a multipeak at 1610 and 3040 cm⁻¹ for the benzene ring and a single peak at 2930 cm⁻¹ for the methylene group. The ¹H NMR spectum of the PS–PEO copolymer showed two peaks at δ 6.4 and 6.9 because of the phenyl ring protons and a single peak at δ 3.5 from the methylene group in the OCH₂CH₂ and a peak at δ 1.4 owing to the C₆H₅CHCH₂ group.

However, the peak in the GPC curve appears somewhat wider than that of the PEO–PS–PEO triblock copolymer, obtained by sequential polymerization of styrene and EO [6]. This increase in peak width is probably because of the poor solubility of α -phenyl ethyl potassium in toluene. DSC studies demonstrated the $T_{\rm m}$ of the PEO block, the $T_{\rm g}$ of the PS block, an exothermic transition of liquid crystals at about 180°C and a single decomposition temperature ($T_{\rm d}$) of the copolymer. However, two $T_{\rm d}$ s occurred for the blend of homopolymers of EO and S.

Quirk et al. [7] synthesized PS–PEO diblock copolymer by functionalizing the living anionically initiated polystyrene with either l-phenyl-l-(l-pyrenyl)ethylene or 2-(l-phenyl)naphthalene, followed by polymerization of EO initiated by the living polystyrene. Fluorescence studies were performed on micellar dilute solutions of the resulting PS–PEO diblock copolymer. The absence of excimer formation and the presence of energy transfer suggests that the fluorescent naphthalene or pyrene labels are separated from each other by relatively large molecular distances.

Calderare et al. [8] synthesized the diblock copolymers bearing anthracene or phenanthrene groups at block junctions by sequential anionic polymerization using cumyl potassium initiator. Labelled copolymers were characterized by UV spectroscopy, GPC and ¹H NMR spectroscopy. Micelle formation in tetahydrofuran-methanol, 1,2-dichloroethane-methanol, tetrahydrofuran-water and water solutions by the diblock copolymer was studied by fluorescence spectroscopy. When micelles containing both donor (phenanthrene) and acceptor (anthracene) groups were present in water, intermicellar nonradiative energy transfer could be observed. For the block copolymer with $M_n = 114\ 000$ and 93 wt.% PEO, they found the onset of spherical micelle formation in water in the range of 10×10^{-3} g/l.

Hazer et al. [9] prepared the diblock copolymer by macroinitiator or macroinimer with terminal

$$CH_3(C_6H_5)CH_2^-K^+ \xrightarrow{styrene} PS^-K^- \xrightarrow{EO} PS^-PEO^-K^+$$

Scheme 4.





double bonds which were prepared from the reaction of 4.4-dicyano-4.4 azovaleryl chloride with PEG ($M_n = 400$) and with either benzyl chloride, acetyl chloride or acryloyl chloride. The bulk polymerization of styrene by the macroinitiator gave soluble PS–PEO block copolymers with molecular weights of 22 000–29 000, while the polymerization of styrene by the macroinimer gave crosslinked PS–PEO block copolymers (Scheme 5).

Huang et al. [10] obtained PS–PEO diblock copolymer by the combination of anionic and photoinduced charge transfer polymerization using *p*-aminophenol as the parent compound. The whole copolymerization was divided into two stages. In the first stage, the amino group of *p*-amino phenol was protected by benzaldehyde first and then reacted with metallic potassium. The phenoxy anion initiated the polymerization of EO. In the second stage, the PEO prepolymer with the Schiff-base end group was deprotected by acidolysis with acetic acid. The recovered amino group and added





benzophenone generated a charge transfer complex which under UV irradiation initiated the polymerization of styrene (Scheme 6).

The block polymer was purified by precipitation with *n*-hexane, extracted with CH₃CN to remove PEO, then extracted again with cyclohexane to remove PS.

The PS–PEO diblock copolymers exhibited characteristic crystalline behavior and some interesting morphological properties. Early in 1969, Lotz and Kovacs [11] investigated the crystalline properties of the block copolymers and indicated their lamellar crystalline structure. Crystal et al. [12] observed that the block copolymer cast from chloroform or ethylbenzene exhibited spherulite structure.

Gast et al. [13] presented a new morphology of PS–PEO block copolymer. Dynamic light scattering and TEM revealed the presence of semicrystalline micelles having both cylindrical and planar geometries. These crystallites always coexist with spherical micelles. The existence of crystallites in the block copolymer is closely related to water content. Dehydrated solutions exhibit crystals that are easily disrupted by small amounts of water. These observations illustrate the interplay between ordering and amphiphilic character in the morphology of assembled block copolymers.

Kelly et al. [14] observed that the PS–PEO diblock copolymer could form a toluene soluble complex with potassium phenolate and used it as a phase transfer catalyst in the Williamson reaction between solid potassium phenolate and toluene solution of alkyl halide.

The aggregation behavior of several PS–PEO block copolymers in pure and mixed solvents was studied by Bahadur et al. [15]. The copolymers were characterized by photon correlation spectroscopy, viscosity and turbidity methods. Various factors affect micelle formation, viz. the molecular characteristics of copolymers, solvent, temperature and inorganic or organic additives. Compact polymer micelles are dissociated or destabilized with an increase in temperature and in the presence of a second solvent, salt or an alcohol.

Wilhelm et al. [16] also studied the block copolymer micelle formation by a combination of fluorescent and quasielastic light scattering techniques. PEO–PS diblock and triblock copolymers with molecular weights 8500–29 000, formed spherical micelles in water. Quasielastic light scattering signals could be detected over the entire concentration range. Pyrene in water (6×10^{-7} M) partitions between the aqueous and micellar phases, accompanied by three changes in pyrene spectroscopy. A red shift in the excitation spectrum, a change in the vibrational fine structure of pyrene fluorescence and an increase in the fluorescence decay time (from 200 to about 350 ns) accompanied the transfer of pyrene from an aqueous to a hydrophobic micellar environment. From these data, critical micelle concentration and the partition coefficient were calculated to be 1–5 mg/l and 3×10^5 , respectively.

Xu et al. [17] studied the micellization behavior of the diblock copolymer in aqueous solution via static and dynamic light scattering techniques. There are two narrowly distributed populations which do not change over the concentration range of $2 \times 10^{-5}-2 \times 10^{-3}$ g/ml. The weight fraction of larger particles decreases with increasing polymer concentration. The small particles are regular micelles with an association number of several hundred. The large particles are loose micellar clusters of tens of micelles. The micelle structure is core-shell with a core of PS and shell of PEO. They also found that when an AB diblock copolymer is placed in a good solvent for the A block but a nonsolvent for the B block, the molecules associate to form micelles. These micelles are nomally spherical in shape with a core rich in B chains surrounded by a corona of A chains swollen by the solvent.

PS–PEO di- or triblock copolymer micelles of various compositions and molecular weights in water were further investigated by light scattering [18]. Characteristic micelle size (hydrodynamic radius R_h) were resolved from a secondary association by a combination of static and quasi-elastic light scattering

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signals. The R_h values for the micelles are in good accord with the scaling relationship of Halperin's star model. The star model was incorporated into the data analysis to obtain an aggregation number and core radii. With these parameters it is possible to test the validity of the Neolandi–Hong mean density micelle model by using their equations to calculate the Flory–Huggins χ parameter for the interaction of PEO– H₂O and PEO–PS. The χ values obtained are in very good agreement with values reported in the literature. A monotonic dependence of χ_{PEO-H_2O} on PEO concentration was found.

A fluorescence method was described by Wang and Quirk [19] for the measurement of the rate of exchange of chains between micelles formed by diblock copolymers in aqueous solution. The method requires two samples of the diblock copolymer. One sample was labelled with a Foerster donor and the other with a Foerster acceptor. Successful application of the method was demonstrated with PS-PEO diblock copolymers. The donor and acceptor are naphthalene and pyrene, respectively. The label is covalently attached to the copolymers at the junction points between the two blocks. Solutions with micelles are formed independently by the two labelled samples. At the time of mixing of the two solutions no micelle contains both a donor and an acceptor. Micelles containing both types of labels may be formed at later time as a consequence of the exchange of labelled chains. The efficiency of nonradiative singlet energy transfer from naphthalene to pyrene was measured as a function of time after mixing of the two solutions. At 60° C, the rate constant deduced from the time dependence of the fluoresence is of the order of 10^{-5} s^{-1} .

An ellipsometric study [20] of a PS–PEO block copolymer at the air-water interface over surface fractional coverage $0.007 \le \theta \le 1$ showed that the copolymer formed a macroscopically homogeneous monolayer over the entire range of θ . The phase angle difference was directly proportional to θ over a wide range, in agreement with microscopic theories based on independent molecular polarizability.

Tripp and Hair [21] studied the adsorption of three PEO–PS block copolymers on silica particles suspended in CCl₄. The three block copolymers differ in the relative sizes of the PEO and PS blocks. Although CCl₄ is a good solvent for both PEO and PS, the PEO segments of the block copolymer were preferentially adsorbed on the surface OH groups (silanol), because the segment/surface interaction of PEO is stronger than that of PS. With an excess of polymer in the solution all three copolymers stabilize the silica dispersion. However, at this concentration the PEO segments may not be adsorbed exclusively because of the geometric constraints imposed by the relative block sizes. At lower polymer concentrations the relative number of PS segments adsorbed on the surface sites is higher as a result of the formation of interparticle bridges. Flocculation occurs because the PS segments extending from the surface of one particle form interparticle bonds by attaching to exposed silanol sites on other silica particles. Redispersion can be induced by adding a small displacer molecule (e.g., triethylamine) to selectively cleave PS/silanol interparticle bonds.

Tripp and Hair also used IR spectroscopy to present direct evidence of the dynamic behavior of segment/surface interaction [22]. The time dependent behavior of the segment/surface interaction of a PS-PEO block copolymer adsorbed on silica particles was reported. Three distinct zones were identified. In the first region, the polymer adsorbs on vacant sites on the surface and does not undergo any rearrangement. The relative number of surface-anchored PEO and PS segments was dictated by each block size. In the second region, the surface sites are fully covered and fresh polymer arriving at the surface is accommodated by a rearrangement of the existing adsorbed polymer layer. The more weakly attached PS segments are replaced by PEO units of the incoming chains. In the final stage, a slow rearrangement of the adsorbed polymer layer occurs. The adsorbed PS segments are sacrificed as additional adsorbed layers tend toward the brush conformation.



Scheme 7.

Riess [23] indicated that block copolymers with PEO contents of 60%-80% were preferred as surfactant for oil-in-water emulsions, while for stable water-in-oil emulsions, copolymers having a 60%-80% PS content were efficient.

2.2. PEO-PS-PEO triblock copolymers

Szwarc [24] first reported the synthesis of a PEO–PS–PEO block copolymer (BAB type), using a sequential anionic polymerization of styrene and EO in tetrahydrofuran initiated by naphthalenyl sodium. Finaz and Rempp [25] described the preparation of BAB block copolymer with a disodium compound of a-methylstyrene tetramer as the initiator. Zgonnik [26] used biphenylpotassium as the initiator and tetrahydrofuran as the solvent in a sequential polymerization of S and EO to form a BAB block copolymer. A dipotassium compound of α -methylstyrene tetramer was used by Marti [27] for the preparation of the same type block polymer.

Nair et al. [28] obtained PEO–PS–PEO copolymers by converting one terminal OH groups of PEG to secondary amine and then to thiuram disulfide via thiocarbamylation. The amine-terminated polyether iniferters were then used as polymeric initiators for styrene. PEO–PS–PEO triblock copolymers were thus prepared (Scheme 7).

PEO–PS–PEO triblock copolymers were synthesized by Xie et al. [6] through sequential dianionic polymerization of styrene and EO in toluene using alkali metal naphthalene as initiator as shown in Scheme 8.

The results showed that the activity of alkali metal naphthalenes decreased in the following order:potassium naphthalene > sodium naphthalene > lithium naphthalene. The last of these barely initiates the block copolymerization of EO with the PS anion. If EO was polymerized first and then styrene added, the latter could not be polymerized, as the reactivity of the alkoxide anion is less than that of styrene. In block copolymerization, the polymerization rate of EO is far less than in homopolymerization and much longer time was needed to reach high conversion.

In the course of this block copolymerization a strange phenomenon was observed [29]. After adding EO to living polystyrene in toluene and copolymerizing at 60°C for 8 h, bead-like particles appeared uniformly suspended in the copolymerization system. The particles disappeared after shaking and

$$K^{+}SS'K^{+} \longrightarrow K^{+}PS'K^{+} EO \longrightarrow K^{+}PEO PS PEO'K^{+}$$

Scheme 8.

reappeared after setting at 60°C. This phenomenon was closely related to the block lengths of PEO and PS.

When the molecular weight of either block was too small, only a homogeneous solution of amber color was observed. No such phenomenon appeared for mixed solution of hompolymers with almost the same molecular weight as the blocks. When the copolymerization was terminated, the solution was poured into a culture dish and warmed under an infrared lamp. After a few minutes of heating, a polygonal network of lines appeared on the surface of the solution, which disappeared on shaking and reappeared on setting. Even after the block copolymer was purified, its toluene solution still showed this unusual mesomorphic phenomenon.

This is probably because of a repelling effect produced by thermodynamic incompatibility between hydrophilic polyoxyethylene blocks and hydrophobic polystyrene blocks and the resulting formation of domains of hydrophilic crystallizable polyoxyethylene blocks and hydrophobic polystyrene blocks. When light is passed through the solution with these two dissimilar domains, refraction of light occurs. When the molecular weight of one block was sufficiently small, it was difficult to form domains, hence homogeneous solutions of amber color resulted. If the polymerization system was stirred, the block domains were destroyed and the system exhibited no suspended beads. The polygonal network line appearance on the surface of the solution perhaps was also because of the domain state of the triblock copolymer.

Water and cyclohexane were used separately for extracting the homopolymers of EO and styrene from the block copolymer. The efficiency of the extractions was evaluated. Two extractions for each solvent efficiently separated the homopolymers from the copolymer. According to GPC results, the elution count (V_c) of PS was 46, and its molecular weight distribution was narrow. However, after block copolymerization with EO, the V_c shifted to 43, which indicates a molecular weight increase and the disappearance of PS after extraction. The ¹H NMR spectrum of the copolymer indicated that the two peaks at δ 6.4 and 6.9 are caused by the phenyl ring protons, the single peak at δ 3.5 from the methylene group in the – OCH₂CH₂– and the peak at δ 1.4 is because of the C₆H₅–CHCH₂– group. Thus, the purified polymer contains both styrene units and oxyethylene units. Torsional braids analysis curve showed two maxima at 56°C and 93°C corresponding to the T_m of PEO and T_g of PS. All these results indicate that the purified polymer is truly a block copolymer.

Two diffuse diffraction rings were observed in the electron diffraction pattern of a triblock sample with $\bar{M}_{nPS} = 41\ 400\ \text{and}\ \bar{M}_{nPEO} = 37\ 000$. The small angle laser light scattering H_v pattern exhibited diffuse four leaves. A TEM micrograph showed a rod-like aggregate aligned somewhat parallel, indicating that the blocks exist in lamellae.

A toluene solution of the triblock copolymer (10 wt.%) was a viscous liquid. When poured onto a glass plate, it took days to dry. In comparison, the viscosity of solution of the hompolymers mixture was lower and the dried film formed only after several minutes. Under polarized microscope, the triblock copolymer with $\bar{M}_{nPS} = 12\ 700$ and $\bar{M}_{nPEO} = 10\ 000$ in toluene solution exhibited a change from transparent and isotropic to a phase-separated anisotropic form with the increase of copolymer concentration. The depolarizing effect increased with the increase of copolymer concentration.

Triblock copolymers consisting of two terminal blocks of comblike polymethacrylate with oligo(oxyethylene) (average degree of polymerization 8) side chains and a middle block of PS were synthesized by successive anionic polymerization of styrene, followed by copolymerization with oligo(oxyethylene) methacrylate [30]. The polymers were then solution cast from tetrahydrofuran solutions of LiClO₄. The homogeneous solvent-free polymer electrolyte systems were tested for conductivity and their thermal



characteristics studied by DSC. The inclusion of a PS block in the comblike polymethacrylate electrolyte vastly improved film formation and mechanical properties, but also lowered the conductivity. Addition of MeO(CH₂CH₂O)₄Me enhanced the ion conduction which could reach values of 10^{-4} S/cm at 70°C depending on salt and PS content.

2.3. PS-PEO-PS triblock copolymers

The PS–PEO–PS triblock copolymer (ABA type) cannot be obtained directly by anionic polymerization because of the weak reactivity of the PEO anion, which cannot initiate the polymerization of styrene. Therefore, Finaz and Rempp [25] reported the synthesis of an ABA block copolymer by treating the PS anion with an excess of $COCl_2$ in toluene. This mixture was then reacted with polyethylene glycol in the presence of pyridine (Scheme 9).

This type of copolymer was also prepared by Orhan [31] via a reaction of polyethylene glycol with a diisocyanate to form the isocyanate-capped prepolymer. The NCO group was then reacted with dihydroperoxide to peroxycarbamate, which then initiated radical polymerization of styrene (Scheme 10). Obviously, the product obtained by radical polymerization had a wide molecular weight distribution and contained homopolymer from chain transfer.

Triblock copolymers, PS–PEO–PS, were also prepared by Uyanik et al. [32] through reaction of dihydroxyl-terminated PEO with isophorone diisocyanate and then with *t*-BuOOH. The resulting polymeric peroxycarbamates were used as free radical initiators for polymerization of styrene. As the PS contents of the samples are lowered, tensile strength, Young's modulus and yield values decrease, while ultimate elongation increases and yield plateaus extend.

Seiler [33] obtained the same type of copolymer by coupling an AB block copolymer with one hydroxyl end group and using butadiene diepoxide as the coupling agent. Lundberg [34] combined an OH-group containing PS with polyethylene glycol (PEG) by using 2,4 toluene-diisocyanate (TDI) as the coupling agent in the synthesis of a PS–PEO–PS copolymer.

Xie and Zhou obtained the PS-PEO-PS block copolymer by coupling PS-PEO block copolymer

Scheme 10.

 $PS-PEO'K^* \xrightarrow{H^*} PS-PEO-OH \xrightarrow{TDI} PS-PEO-PS$

Scheme 11.

with toluene 2,4-diisocyanate [6] (Scheme 11). The crude product can be purified by fractional precipitation, using toluene as solvent and petroleum ether as precipitant. The condition under which the diblock copolymer just began to precipitate was determined, then the crude triblock copolymer was fractionally precipitated at this condition. At the precipitation point most of the diblock copolymer remained in the solution, whereas most of the precipitate was the triblick copolymer. The M_n of one sample of the diblock copolymer was determined by membrane osmometry to be 2.75×10^4 and after coupling with toluene 2.4-diisocyanate it became 5.84×10^4 . The ratio of these two M_n s is 2.12.

The difference in emulsifying properties of the block copolymers in the water/toluene system was measured by using a conductometric method [6]. An emulsion was formed by adding water to the toluene solution. When the emulsion changed from the oily continuous phase to aqueous continuous phase, an abrupt rise in conductivity was detected. The conductivity began to fall when the amount of water added reached a critical value, over which the emulsion was destroyed, and phase separation into two layers resulted. The critical amount of water added per definite weight of copolymer was defined as the emulsifying ability of the block copolymer. The results indicated that the emulsifying ability of the block copolymer. At a similar PEO content, M_n and concentration, the emulsifying ability decreases in the following order: PEO–g-PS > PEO–PS–PEO > PEO–PS > PS–PEO–PS.

This difference is probably because of the following reasons. In the PEO–PS–PEO block copolymer, the PEO blocks are at both ends of the chain and easily interact with water. In the PS–PEO or PS–PEO–PS block copolymers, the PEO block is shielded by the PS block at one end or two ends of the chain, and the emulsifying ability is reduced. In the graft copolymer, hydrophobic PS grafts of equal length are distributed along the hydrophilic PEO chain. When water is added to this toluene solution, the PEO chain is probably in a ring-like structure in the toluene solution. Therefore the hydrophobic grafts are arranged outside the ring and water is included within the ring. Hence, the emulsifying ability is enhanced.

Xie and Zhou showed that crystallinity of the block copolymers determined by WAXD increases with PEO content and decreases in the following order [6]: PEO-PS-PEO > PS-PEO > PS-PEO-PS. Perhaps in the PS-PEO-PS triblock copolymer amorphous PS blocks at the ends of the PEO block limit the folding of the PEO block. In the PEO-PS-PEO copolymer, however, the PEO blocks situated at the ends of the chain can be folded more freely and easily. Thus, crystals can be formed more completely.



Scheme 12.

 $2PS^{-}Li^{+}+SiCl_{4} \longrightarrow (PS)_{2}SiCl_{2} \longrightarrow (PS)_{2}Si(PEO)_{2}$ $2PS^{-}Li^{+}+SiRCl_{3} \longrightarrow (PS)_{2}SiRCl_{2} \longrightarrow (PS)_{2}SiR(PEO)$

Scheme 13.

2.4. Star-shaped block copolymers of S and EO

Huynh Ba-Gia et al. [35] obtained star shaped $PS-(PEO)_2$ block copolymer through polymerization of EO using a dianionic initator formed by metallation of naphthalene-terminated PS with potassium (Scheme 12).

Lutz and Rempp [36] synthesized star-block copolymers using a multifunctional organometallic initiator which was obtained upon reaction of potassium naphthalene with divinylbenzene (DVB). In a subsequent step the core sites initiate the polymerization of styrene or EO to yield star-shaped block copolymer of PEO and PS. The major advantage of this synthetic method is that it allows functionalization of the branches at their ends, thus providing the possibility of further reaction or polymerization with other monomers.

Electron transfer initiation by potassium naphthenide was selected to make the poly-DVB cores at high dilution in a polar solvent (THF) [37]. Advantage is taken of the low rate of the electron transfer process, but the molar ratio DVB/K^+ must be kept below 3, in order to avoid formation of microgel. Under these conditions the multifunctional cores do not aggregate. The dilute solution of poly-DVB cores is used to initiate the polymerization of styrene. Subsequently, EO is added and its polymerization is initiated by the carboanionic sites at the outer ends of the branches. An immediate gelation was observed as a result of strong association between the alcoholate functions. The chain ends were deactivated protonically leaving alcohol moieties at the outer ends of the branches. These PS–PEO star-block copolymers exhibit amphiphilic behavior and tend to give stable emulsions in water.

Rempp et al. [38] also pointed out that electron-beam irradiation of the star polymer leads to hydrogel which with higher styrene content shows no swelling.

Tsitsilianis et al. [39] obtained heteroarm star copolymers bearing PS and PEO branches by sequential anionic living copolymerization. The synthesis involves three steps. In the first step a living polymer precursor is formed, which is subsequently used to initiate the polymerization of a small amount of a suitable bis-unsaturated monomer (divinyl benzene). A living star-shaped polymer is formed, in which the number of active sites is equal to the number of branches. In the third step these active sites are used to initiate the polymerization of another monomer of suitable electroaffinity. New branches of a different kind then grow from the core, yielding the heteroarm star copolymer. A drawback of this method is that the functionality cannot be predicted. However, many experimental results are available and can be used to approach the desired values. The functionality of the stars is influenced mainly by the molar ratio of divinylbenzene per living ends and the molecular weight of the linear PS precursor. These star copolymers exhibit association phenomena not only in water but also in tetrahydrofuran, which is not a selective solvent for the different arms. The PEO arms can be crystallized, forming well-defined spherulites.

Xie and Xia prepared the star-shaped block copolymers with two arms of PS blocks and two arms of PEO blocks by coupling living PS anions first and then living PEO anions using SiCl₄ as the coupling

agent and the star-shaped copolymers with two arms of PS blocks and one arm of PEO block using CH₃SiCl₃ as the coupling agent [40] (Scheme 13):

When SiCl₄ was dropped into a solution of PS anions, the red color of the anion did not disappear even at a SiCl₄ : PS anion ratio of 1 : 4. GPC analysis showed that only half of the PS anions were coupled. But when the ratio of SiCl₄ : PS anions reached 1 : 2, the red color disappeared, and the GPC trace indicated a product having the double molecular weight of the PS anion. These results imply that only two atoms of chlorine in SiCl₄ can be exchanged with PS anions, probably because of steric hindrance. However, when PEO anions are coupled by SiCl₄, all four chlorine atoms can react with the anions. This result is consistent with the relative steric requirements of the two anions.

Purification of the block copolymers is better carried out by first dissolving the crude product in toluene, then extracting the solution with a large amount of water to remove the homopolymer of EO. This method prevents the loss of block copolymer during extraction with water. After evaporation of toluene, styrene homopolymer can be removed from the residue by extraction with diethyl ether. The purified star-shaped block copolymers are white, stable solids, which are soluble in benzene, toluene, tetrahydrofuran or chloroform, but only slightly soluble in water, ethanol or diethyl ether.

GPC curves indicated that $(PS)_2(PEO)_2$ from SiCl₄ and $(PS)_2$ (PEO) from CH₃SiCl₃ are rather pure, while $(PS)_2(PEO)$ from SiCl₄ contained a small amount of $(PS)_2(PEO)_2$. Molecular weight values of the purified $(PS)_2(PEO)_2$, determined by GPC, fit well with the values calculated on the basis of the molecular weight of PS and PEO precursors.

Both IR and ¹H NMR spectrum confirmed that the purified copolymer contains both monomeric units of S and EO. Torsional braid analysis of the purified copolymers indicated that two transition temperatures appear at 56°C and 93°C, corresponding to the T_m of PEO and T_g of PS. This implies the occurrence of microphase separation and also indicates that the purified copolymer is truly a block copolymer.

Crystallinity of the purified star-shaped block copolymers increases with the PEO content or with the molecular weight of the copolymers. When the copolymer is quenched in petroleum ether at 20°C, spherulites, observed under polarized microscope, seem to be more regular than those of the copolymer quenched at 0°C. Probably there was insufficient time for the PEO units to crystallize regularly into spherulites at 0°C. The spherulites were regular when the copolymer was cast from chloroform rather than from ethylbenzene, as chloroform is a good solvent for both PEO and PS blocks, while ethylbenzene is a good solvent for PS blocks, but a poor solvent for PEO blocks. These star-shaped block copolymers exhibit the same peculiar mesomorphic behavior in toluene solution as PEO–PS–PEO triblock copolymers.

Huynb-Ba-Gia et al. [35] studied the emulsifying properties of their star-shaped block copolymers of S and EO using emulsifying volume to express the emulsifying properties. The emulsifying volume was taken as the total volume of water plus the benzene solution of the copolymer before mixing minus the volume of water separated after thoroughly mixing and then settling.

The study of the emulsifying volume of the star-shaped block copolymers synthesized by Xie and Xia [40] showed that at constant amount and percentage of PEO in the copolymer, the smaller the molecular weight of the copolymer, and the higher the number of arms, the larger the emulsifying volume. This may be explained by the increase of emulsifying centers as the molecular weight of the copolymer decreases. The emulsifying volume increases with PEO content of the copolymer within a certain limit.

UV absorption indicated that the star-shaped block copolymers could complex with alkali metal picrates [40]. After addition of increasing amounts of the copolymer to a lithium picrate solution in

tetrahydrofuran, the absorption maximum shifted to a larger and larger wavelength until it reached a particular value. The absorption spectra can be classified in two groups. The first group of spectra with a maximum absorption at relatively shorter wavelength (about 340 nm) in the presence of smaller amounts of copolymer indicates a complex of lithium bound peripherally by the PEO units. The second group of spectra with a maximum absorption at longer wavelength (about 375 nm) in the presence of larger amount of copolymer is attributed to the formation of a second complex, in which the PEO units are inserted into the ion pairs of the salt. Similar changes of the UV absorption at 380 nm. The maximum absorption wavelength of the lowest absorption peak for the picrates of lithium, sodium and potassium is located at 357, 363 and 366 nm, respectively.

Lithium picrate is slightly soluble in chloroform or toluene, while sodium or potassium picrates are insoluble. Addition of the star-shaped block copolymer enhances the solubility of the alkali metal picrates in chloroform or toluene. The order of enhancing solubility of the alkali metal picrate in toluene is: star-shaped block copolymer > diblock copolymer > PEO. The star-shaped block copolymer with PEO contents of 40%–50% exhibits the largest effect. The solubility of alkali metal picrates, complexed with the copolymer in toluene, decreases in the following order: Li > K > Na.

As the PEO–containing copolymers can complex with alkali metal picrates, they were tried as phase transfer catalysts in the Williamson reaction. They evidently increase the yield of the reaction between solid potassium phenolate and *n*-buty bromide in toluene, The order of catalytic efficiency is: star-shaped block copolymer > diblock copolymer > PEO. The catalytic efficiency increases with the molecular weight of both the PEO block and the PS block.

Ionic conductivity of salt complexes of the star-shaped copolymers of EO and S were studied by Xie et al. [41]. At a CH₂CH₂O/cation ratio or EO/M = 20 all the Arrhenius conductivity plots consist of two straight-line regions with a discontinuity at a temperature range between 45°C and 60°C. Below 45°C the crystalline phase of PEO, the amorphous phase of PEO with dissolved salt and the polystyrene phase may exist together. DSC analysis demonstrated the endothermic melt peak of PEO, T_g of the polystyrene phase and also T_g of the PEO complex. In the temperature range of 45°C–60°C, the crystalline phase of PEO melts gradually or changes into an amorphous phase complexed with cations, thus markedly enhancing the cation transport and increasing the conductivity. The conductivity increases gradually with further rise in temperature owing to reduction of viscosity of the PEO melt. For the KCNS complex of the star-shaped block copolymer with EO/K = 20, the conductivity reaches the value of 2×10^{-5} S/ cm at 25°C. At EO/K = 4.5 the Arrhenius plot is linear from room temperature to 100°C. This implies that no phase transition from crystalline PEO to amorphous PEO occurs.

The conductivity decreases in the following order of cations: $K^+ > NH_4^+ > Na^+$. The DSC curves indicated that the T_m of the crystalline PEO in the NaCNS complexes decreases with decreasing EO/Na ratio, until the T_m of PEO disappears at EO/Na = 4 and the T_m of the crystalline complex appears. The same phenomenon was observed by WAXD.

At about the same PEO content of the copolymer and EO/Na = 20, the less the molecular weight of PEO arms, the higher is the conductivity of the NaCNS complex. This is ascribed to the lower crystallinity of the copolymer with lower molecular weight of PEO. If the molecular weight of the PEO arms in the copolymer is kept almost constant, conductivity decreases with reduction of PEO content, as too much polystyrene, especially more than 60%, will make the PEO phase become discontinuous, restricting the cation transport through the copolymer complex and thus resulting in decrease of room temperature conductivity. It is very interesting to reveal that the FeCl₂ complex exhibits conductivity even higher than NaCNS but lower than KCNS. γ -Butyrolactone exerts significant influence on the conductivity of the NaCNS complex of the star-shaped block copolymer. On addition of 25% γ -butyrolactone the room temperature conductivity increases about 2.5 orders of magnitude, reaching the value of 2×10^{-4} S/cm at 25°C. γ -Butyrolactone plays a role of plasticizer, increasing the polarity of the medium and decreasing the viscosity and the crystallinity of PEO, thus enhancing the ionic conductivity. DSC studies demonstrated that with increasing amount of γ -butyrolactone added, not only $T_{\rm m}$ and $T_{\rm g}$ of the PEO complex, but also $T_{\rm g}$ of the polystyrene arms decreased. Thus γ -butyrolactone enhances the mobility of both the PEO segments and the PS segments.

The star-shaped block copolymers of S and EO can be used as compatibilizers for blending epichlorohydrin rubber and polystyrene. Mechanical properties of unvulcanized epichlorohydrin rubber are rather poor. The material possesses low tensile strength and very large ultimate elongation and permanent set. Blending this rubber with 30% polystyrene increases the tensile strength but decreases notably the ultimate elongation down to less than 100%. Addition of 2% star-shaped block copolymer of S and EO to the blend not only increases the tensile strength, but also raises the ultimate elongation and decreases the permanent set. This demonstrates that the star-shaped block copolymer of EO and S enhances the interfacial adhesion of the two phases with two arms of PS blocks distributed in the PS phase and with two arms of PEO blocks distributed in the epichlorohydrin rubber phase.

2.5. Multiblock copolymers containing PEO and PS segments

Shimura and Lin [42] synthesized oxyethylene-styrene multiblock copolymers by coupling α,ω dihydroxypolystyrene with polyethylene glycol (PEG) using 4,4-diphenylmethane diisocyanate as coupling agent. Films cast from benzene solutions of products were soft and elastic, showing a tensile strength of 13 MPa and 44% elongation.

Booth and his coworkers [43] prepared oxymethylene-linked PEO by reaction of dichloromethane with PEG (molecular weight 400) in the presence of KOH. The conductivity of its complex with LiCF₃ SO₃ reached 4×10^{-5} S/cm at 20°C. Two years later the same workers [44] used dichloromethane, KOH, PEG (molecular weight 400) and monohydroxyl-terminated PS to prepare oxymethylene linked PEO–PS multiblock copolymer, and showed that its complex with LiCF₃SO₃ had a conductivity lower than 1×10^{-5} S/cm.

Cakmak [45] synthesized multiblock copolymer of MMA, S and EO by redox polymerization of MMA using Mn^{2+} and PEG having azo and hydroxy functions, followed by free radical polymerization of styrene through thermal decomposition of the azo groups, resulting in the formation of multiblock copolymer. Successful blocking was confirmed by fractional precipitation, a strong change in the molecular weight and spectral measurement.

Xie et al. [46] reported the synthesis of urethane-linked PEO–PS and PEO–PS–PPO(polyoxypropylene) multiblock copolymers by coupling PEG, PPG (polypropylene glycol) and α,ω -dihydroxypolystyrene with 2.4-toluene diisocyanate. The copolymers were purified by successive extractions with water and ethyl ether. The optimum synthetic conditions are: NCO/OH = 1.1 molar ratio, dibutyl tin dilaurate catalyst/prepolymer = 0.5–0.7 wt.% and 20–25 wt.% prepolymer concentration. The yields of purified copolymers at optimum conditions are 92 ± 3% when the molecular weight of PEG is less than 10 000. The purified copolymers were characterized by ¹H NMR and IR spectroscopy. The composition of purified copolymers determined by ¹H NMR is quite close to that of prepolymer mixture. The

structural parameters were calculated from the molecular weights of the copolymers and prepolymers, determined by membrane osmometry and vapor phase osmometry (VPO), respectively. The results showed that the copolymers consist of more than 30 blocks. The multiblock copolymers exhibit good emulsifying properties, good phase transfer catalytic properties in Williamson reaction and excellent water absorption capacity (higher than 800%). The multiblock copolymers containing 50–60 wt.% PEO blocks offer the best emulsifying properties, because PEO blocks are hydrophilic and both PS and PPO blocks are hydrophobic. The copolymer with about 60 wt.% PEO content display optimum phase transfer catalyst behavior, giving higher conversion of potassium phenolate in the Williamson reaction, as the phase transfer catalyst benefits from the ability of PEO block to complex with K⁺ ions, as well as the ability of hydrophobic blocks to carry the complex into organic phase. The mechanical properties of the multiblock copolymers indicated that they behave like a thermoplastic elastomer or a toughened plastic, depending on the composition, e.g. the copolymer with PS/PEO/PPO = 2/4/4 is a thermoplastic elastomer, whereas that with PS/PEO/PPO = 4/4/3 is a toughened plastic.

Two years later Xie and his coworkers [47] described the synthesis of PEO-PPO-PS multiblock copolymers by coupling PEG, PPG and telechelic dihydroxy-PS, using dichloromethane as coupling agent and KOH as catalyst. The copolymers were purified by extraction with hot cyclohexane and distilled water successively. The purified copolymers were characterized by IR, ¹H NMR, GPC and membrane osmometry and were shown to be multiblock copolymer containing more than 100 blocks. The crystallinity of the copolymers varied from 12% to 32%. The crystallinity increases with molecular weight and content of PEO and decreases markedly when the copolymer is complexed with LiC1O₄. At the same PEO content, PPO blocks seems to lower the crystallinity more severely than the PS blocks, probably because there is greater compatibility between PEO and PPO than between PEO and PS. The multiblock copolymer containing about 75 wt.% PEO block showed the best emulsifying properties and phase transfer catalytic behavior. At the same PEO content the phase transfer catalytic activity of different multiblock copolymers decreases in the following order: PEO-PS > PEO-PPO-PS > PEO-PPO, whereas conductivity of the LiC1O₄-complexed copolymers decreases in the opposite order. The conductivity of LiC1O₄ complexes of some three component multiblock copolymers reaches above 2×10^{-4} S/cm at 25°C, whereas that of PEO–PPO (95/5) multiblock copolymer reaches 5.8 × 10^{-4} S/cm at 25°C and 1.2×10^{-3} S/cm at 30°C. The tensile strength of the copolymers increases with the content and molecular weight of PS or PEO blocks.

Xie et al. [48]. also prepared styrene–butadiene–oxyethylene multiblock copolymers by coupling telechelic dihydroxyl polybutadiene, telechelic dihydroxyl PS and PEG using 2,4-toluene diisocyanate as coupling agent. The products were purified by successive extractions with hot cyclohexane and water. The purified products were characterized by GPC, IR spectrophotometry, dynamic mechanical spectroscopy, ¹H NMR spectroscopy and transmission electron microscopy and identified to be multiblock copolymers. The structural parameters of the multiblock copolymer, calculated from molecular weights of the copolymer and the prepolymers, determined by membrane osmometry and VPO, respectively, were shown to consist of 40–60 blocks. These multiblock copolymers exhibit very good emulsifying properties in comparison with the aforesaid PEO–PS–PPO multiblock copolymers, even though their water absorbency seems lower (350%). They also possess a good phase transfer catalytic activity in the Williamson reaction. The conversion of potassium phenolate reaches more than 95% at 120°C for 4.5 h, using 10% copolymer(containing 57 wt.% PEO) based on potassium phenolate, whereas only 10% conversion was obtained in the absence of the multiblock copolymers. The LiClO₄ complexes exhibit a conductivity above 1×10^{-4} S/cm at 35°C.

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Scheme 14.

3. Graft copolymers from ethylene oxide and styrene

3.1. PS-g-PEO, graft copolymers with PEO side chains

Candau, Rempp et al. [49] obtained PS–g-PEO by reaction between living monofunctional PEO and partly chloromethylated PS backbone (Scheme 14). Characterization of the products by light scattering, VPO, GPC, UV and NMR spectroscopy showed a high degree of grafting. The products exhibited microemulsifying properties.

Shalati and Overberger [50] synthesized PS–g-PEO by first alkylation of PS of weight-average molecular weight (2.2×10^4) with 4-nitrophthalimidomethyl groups as grafting sites. Several PS with various degrees of grafting sites were prepared and characterized. Living PEO with narrow molecular weight distribution was prepared in the presence of 15-crown-5 and grafted onto the 4-nitrophthalimidomethylated PS. The nitro displacement reaction was fast and the grafting yield was quantitative (100%). The intrinsic viscosities of the graft copolymers are higher than those of the backbone polymers. As the degree of grafting increases, the intrinsic viscosity shows an initial increase, followed by a decrease.

Ito et al. [51] used a macromer technique to obtain graft copolymers with uniform side chains. They synthesized a graft copolymer of PS with uniform PEO side chains through copolymerization of styrene with PEO macromer (Scheme 15).

They obtained PEO macromers using potassium tertiary butoxide as initiator and methacryloyl chloride or *p*-vinyl benzyl chloride as terminating agent. An apparent decrease in the reactivites of both poly(ethylene oxide) macromers and comonomers was ascribed to thermodynamic repulsion between the macromer and the backbone. [52]. An amphiphilic polystyrene–g- ω -stearyl-polyoxyethylene copolymer was prepared using the macromer technique [53]. The graft copolymers were described as microphase separated and can be used in applications that require blood compatibilities and antithrombogenic properties.

Riza et al. [54] obtained PS-g-PEO by dispersion copolymerization of PEO macromer having terminal methacryloyl groups with styrene in the presence of 2,2'-azobis(N,N'-dimethylene-isobutyramide)



Scheme 15.



Scheme 16.

in ethanol/water mixture (4/1 v/v) at various temperatures. The overall activation energy for the dispersion copolymerization was 48 kJ/mol.

Later they [55] studied the dispersion polymerization initiated by a water/ethanol soluble 2,2'-azobis(N,N'-dimethylene-isobutyramide) and oil-soluble benzoyl peroxide at 60°C. The rate of polymerization and the number of polymer particles found increased with initiator concentration. The partition of benzoyl peroxide molecules between the continuous phase and the polymer particles cause the formation of radicals in both phases. The radical fragments located in polymer particles take part in both initiation and termination events. The latter is responsible for the low rates and molecular weight of the graft copolymers.

This type of graft copolymers of S and EO was also obtained by Xie et al. [56] through copolymerization of styrene with PEO macromer, prepared by anionic polymerization of EO in dimethylsulfoxide using potassium naphthalene in tetrahydrofuran as initiator, followed by termination with methacryloyl chloride. The reactions are shown (Scheme 16).

The method of macromer synthesis developed by Xie et al. [57] has the advantage of shorter reaction time and a larger range of molecular weight of the PEO macromer than the usual method using potassium alcoholate as initiator. PEO macromers with molecular weight from 2×10^3 to 3×10^4 and $\bar{M}_w/\bar{M}_n = 1.07-1.12$ can be obtained by this method. The macromers were shown by UV, IR and ¹H NMR to have one double bond per molecule. The methacrylate terminated PEO macromers can be copolymerized with styrene with a reactivity ratio r_2 of 1.32 ± 0.12 which is higher than that of methyl methacrylate during copolymerization with styrene ($r_2 = 0.57$). This is probably because of the larger size of the macromer which reduces the diffusion rate and increases the steric hindrance during copolymerization.

The PS–g-PEO copolymers were purified by extractions three times with diethyl ether and three times with water. GPC analysis of the purified graft copolymer showed that they were free from contamination with the PEO macromer [56].

This type of graft copolymer can also emulsify water/benzene system and enhance the Williamson reaction between solid potassium phenolate and *n*-butyl bromide in benzene. However, in comparison with the graft copolymers of different backbone structures but with the same uniform PEO grafts, the emulsifying ability and phase transfer catalytic efficiency of the copolymer decrease in the order: PMMA–g-PEO > PMA–g-PEO > PS–g-PEO, where PMMA is poly(methyl methacrylate) and PMA poly(methyl acrylate). This may be attributed to the different conformation of the copolymers in benzene solution. The backbone of PS–g-PEO is not very flexible because of the steric hindrance of benzene rings, while the greater flexibility and better water solubility of the PMA and PMMA backbones are more flexible in benzene, results in looser arrangements of PEO grafts in PMA–g-PEO or PMMA–g-PEO and larger probability of contact with water, thus increasing the emulsifying volume. The presence of methyl groups in PMMA–g-PEO makes the backbone more soluble in the organic phase than PMA–g-PEO and thus enhances the emulsifying power of the former. The effect of backbone on the phase



Scheme 17.

transfer catalytic efficiency is also related to the conformation and solubility of the graft copolymers in toluene.

Metallic ion complexes of the graft copolymers exhibit ionic conductivity decreasing in the order: $KCNS > LiClO_4 > FeCl_2$ [41]. For different kinds of copolymers with uniform PEO grafts, conductivity of the complexes increases in the order: PS-g-PEO < PMMA-g-PEO < PMA-g-PEO, while crystallinity of PEO complexes increases in the opposite order: PMA-g-PEO < PMMA-g-PEO < PS-g-PEO.

Poly(*p*-methyl styrene)–g-PEO was synthesized in three stages using a grafting technique [58]. Poly(*p*-methyl styrene) with a controlled molecular weight was first obtained using living anionic polymerization. This polymer was partially functionalized using bromosuccinimide to introduce bromine into the methyl groups on the backbone. Then a coupling reaction of the brominated poly(*p*methyl stryene) with α -hydroxy- ω -methoxy PEO was carried out to produce graft copolymers. The product was used as a polymeric stabilizer in the aqueous emulsion of styrene. The spacing of the PEO side chains on the backbone was found to affect mainly on the efficiency of stabilization.

Bonaccorsi et al. [59] prepared the same graft copolymer from poly(*p*-methyl styrene) with different molecular weights ($M_n = 3000$, 10 000 and 30 000) first metallated by *n*-BuLi-tetramethyl ethylene diamine. The metallated polymer was then reacted wth EO, followed by methanolysis. In the presence of powdered KOH, fixed amounts of EO were polymerized on the alkoxide sites. During application of these copolymers as dispersants in coal water mixtures, the molecular weight of the hydrophobic backbone must not exceed 10 000 and the required length of the hydrophilic branches must be in the range of 90–135 EO units. The hydrophilic–hydrophobic balance value must be in the range of 10–20. The most critical parameter was found to be the density of the hydrophilic chains.

Ballet and Candau studied [60] a microemulsion of PS–g-PEO in toluene– H_2O-2 -propanol using NMR spectroscopy. At low water content the copolymer had a rather diffuse micellar structure in which rotational mobility of oxyethylene units was hardly affected by the ternary solvent. Above a critical water concentration (about 4%) the mobility of oxyethylene chains was restricted, owing to the formation of an inverse micellar structure with water solubilized within the particles. The chemical shifts and linewidths of water protons indicate that most water is initially H-bonded to the hydrophilic part of the graft copolymer and then is present in free form in water aggregates.

Novel graft copolymers with styrene–butadiene–styrene triblock copolymer as backbone and PEO as grafts onto the polybutadiene blocks were synthesized [61] (Scheme 17). The concentration of PEO in



Scheme 18.

the copolymer can be controlled by varying either the number of grafts per molecule or the molecular weight of the PEO grafts. The graft copolymers were combined with LiCF_3SO_3 to form an ion-conducting phase. The conductivities of films of these materials were sensitive to preparation technique and especially to casting solvent. The best conductivities, typically 10^{-5} S/cm at ambient temperature, were likely to induce microphase separation with concomitant improvement in the mechanical properties of the system. The temperature dependence of the conductivity suggested that the materials were essentially amorphous over the range studied.

A novel method [62] utilizing a water soluble carbodiimide was used to chemically graft 100 000 and 615 000 g/mol PEO onto polystyrene latex particles with mean diameter of 375 and 347 nm. Electrophoretic mobility measurements showed that the PEO was truly grafted and not just absorbed. Capillary viscometry measurements yielded a layer thickness of 23 nm for grafted PEO with molecular weight of 615 000. Steady shear and oscillatory rheological measurements indicated a transition from primarily liquid-like behavior to solid-like behavior at an effective volume fraction between 0.528 and 0.550. The rheological behavior was interpreted in terms of long-range repulsive particle interactions because of the grafted polymer layers.

3.2. PEO-g-PS, graft copolymers with PS side chains

Only Xie and his coworkers have published reports concerning the synthesis of PEO copolymer with uniform PS grafts [63], obtained through copolymerization of epoxy ether terminated polystyrene macromer with EO in toluene using *i*-Bu₃Al-H₂O-H₃PO₄-dimethyl aniline (DMA) as catalyst. The epoxy ether terminated polystyrene was prepared by termination of living polystyrene anion with epichlorohydrin in cyclohexane. Synthesis of the macromer and its copolymerization with ethylene oxide are briefly denoted in Scheme 18. The actual wt.% of PS containing epoxy end group in the macromer only amounts to 35% owing to some side reactions between epichlorohydrin and the polystyrene anion.

According to the grafting efficiency or conversion of the macromer, the quaternary catalyst (*i*-Bu₃Al-H₂O-H₃PO₄-DMA catalyst) seems to be more effective than Vandenberg catalyst (*i*-BuAl₃-H₂O-ether)or bimetallic oxoalkoxide catalyst, (RO)₂AlO-Zn-OAl(OR)₂. The optimum ratio of the four components of the quarternary catalyst is *i*-Bu₃Al : H₃PO₄ : H₂O : DMA = 1.0 : 0.15 : 0.15 : 0.10. The grafting efficiency increased with the amount of catalyst used, up to about 3% based on the total amount of EO and the macromer.

The grafting efficiency decreased with the increase of molecular weight of the macromer. This is attributed to the increase of viscosity and steric hindrance caused by the increase of molecular weight of the macromer. The grafting efficiency diminished as the macromer concentration increased. Evidently, this is caused by the lower reactivity and larger steric hindrance of the macromer as compared to EO, when higher concentration of the macromer was used in the copolymerization.



The rate of individual conversion of the macromer is much slower than that of EO, probably because of the smaller mobility and larger steric hindrance of the macromer. After most of EO is consumed, the phenyl content of the product increases gradually with copolymerization time. As the PS macromer does not homopolymerize easily owing to steric hindrance and the quaternary catalyst has a long life with chain transfer, competition of the macromer with PEO molecules for reaction with active center may occur, resulting in more or less redistribution of polystyrene grafts.

The graft copolymer can be purified by successive extractions with hot cyclohexane and with 20% ethyl alcohol which is better than water for extraction. The IR spectrum of the purified graft copolymer exhibited a strong absorption peak at 1120 cm⁻¹, a multipeak at 1610 and 3040 cm⁻¹ and a peak at 2930 cm⁻¹ which are characteristic of the ether linkage, phenyl ring and methylene group, respectively. Torsional braid analysis showed the melting temperature of PEO crystals and the T_g of PS which indicates microphase separation in the graft copolymer.

Average grafting number (N_g) of the purified graft copolymer can be calculated by the following equation:

$$N_{\rm g} = rac{M_{
m nc} imes W_{
m g}}{M_{
m ng}}$$

where $M_{\rm nc}$ and $M_{\rm ng}$ are the number average molecular weight of the copolymer and the macromer determined by membrane osmometry and vapor pressure osmometry, respectively, whereas $W_{\rm g}$ is the weight fraction of polystyrene in the copolymer. Average grafting number of these graft copolymers were determined to be 4–8.

The emulsifying ability of this graft copolymer is higher than that of the block copolymers at the same PEO content as mentioned in Section 2.3. The graft copolymer can absorb a large amount of water, up to 24 moles per PEO segment. Water absorption converts the copolymers from a white hard solid to an elastomer. As absorbed water increases the distance between PEO chains and reduces the crystallinity of PEO, the PEO segment becomes flexible and the hydrophobic polystyrene grafts aggregate into domains resulting in a network.

Recently Xie et al. [64] prepared PEO–g-PS via grafting styrene from the unsaturated PEO, which was obtained by copolymerization of EO with allyl glycidyl ether in toluene using bimetallic-oxoalkoxide as catalyst. WAXD showed that the crystallinity of the unsaturated PEO decreased obviously with increasing amount of allyl glycidyl ether used in the copolymerization. The room temperature conductivity of the LiClO₄ complex of the unsaturated PEO showed a maximum value of 1×10^{-4} S/cm at about 65% PEO content and EO/Li = 20/1. The unsaturated PEO was graft copolymerized with

styrene using AIBN as initiator in toluene with grafting efficiency above 50% (Scheme 19). The grafting efficiency diminishes as the charging amount of the unsaturated PEO increases. The graft copolymers were purified by successive extractions with 20% ethanol and hot cyclohexane and characterization by IR and ¹H NMR indicated both of PEO and PS units. Crystallinity of the graft copolymers decreases with decreasing PEO, while conductivity of their complexes with LiClO₄ at 25°C exhibits a maximum value of 1×10^{-4} S/cm for the graft copolymer containing 70 wt.% PEO. This is because when PEO content is over 60%, decreasing crystallinity increases room temperature conductivity. But when PEO content is lower than 60%, PEO cannot form the continuous phase and hence the ionic conductivity diminishes drastically. LiClO₄ complexes of the graft copolymer with 70% PEO content exhibit a room temperature conductivity approaching 1×10^{-4} S/cm at a molar ratio of EO/Li = 20/1. The graft copolymers exhibit good emulsifying properties and phase transfer properties. The graft copolymer containing about 70% PEO showed the best emulsifying properties and phase transfer catalytic properties, as both PS and PEO segments play a role in emulsification and phase transfer action.

As mentioned before, the various types of multicomponent copolymers of EO and styrene have been designed, synthesized, characterized and their physical properties studied. In the following section, the multicomponent copolymers of EO and alkyl (meth)acrylate will be reviewed.

4. Block copolymers from ethylene oxide and alkyl (meth)acrylate

Seow et al. [65] indicated that living poly(alkyl methacrylate) anions can initiate the polymerization of ethylene oxide. While this method might allow the preparation of block copolymers with well defined molecular weight composition and structure, the addition of EO to living poly(alkyl methacrylate) anions involves potential complications. Side reactions between living PEO and the alkyl ester group of poly(methly methacrylate) block cause the formation of inhomogeneous block copolymers.

However, as reported by Suzuki et al. [66], alkyl methacrylate may be effectively polymerized by initiation with disodium alkoxides of PEG in THF, probably because the nucleophilicity of the polymer dianions is somewhat increased by complexation of the counterions with the polyether chain itself.

The synthesis of block copolymers through addition of MMA to living PEO involves at least two difficulties as indicated by Gary et al. [67] First, the low solubility of the PEO sequence in THF only permits MMA polymerization at temperatures above 20°C, whereas anionic polymerization of MMA in THF only proceeds cleanly below -75° C. Above 20°C, transfer and termination reactions cannot be prevented during the MMA polymerization. Secondly, Suzuki et al. [66] reported transesterification reactions between PEO anion and MMA monomer, resulting in grafted block copolymers.

Reuter et al. [68] synthesized diblock copolymers of EO and *t*-butyl methacrylate (*t*BMA) through sequential anionic polymerization, using cumyl potassium as initiator in THF, as *t*BMA is not as sensitive to side reactions as MMA at room temperature, and the anionic polymerization of *t*BMA in THF at room temperature leads to narrower molecular weight distribution ($M_w/M_n = 1.4-1.7$). By repeated alternate addition of these monomers multiblock copolymers were produced.

The electron micrograph of PEO–PtBMA diblock copolymers composed of blocks of equal sizes exhibits a lamellar structure as expected for block copolymers with equal sequence length. The block copolymers are amphiphilic and influence the interfacial tension of trichloroethylene/water system. The interfacial activity depends not only on the ratio of the sequence lengths and the molecular weights of the polymers, but also the type of block copolymers.



PMMA-PEO-PMMA

Scheme 20.

Wang, Teyssie et al. [69] prepared well defined AB, ABA, BAB block copolymers of *t*BMA (A) and EO (B) by sequential living anionic polymerization of the two comonomers irrespective of addition order, using $(C_6H_5)_2$ CHK and K naphthalene as mono- and difunctional initiators, respectively. For all block copolymers molecular weight distribution was relatively narrow. Results of GPC, selective extractions of homopolymers and NMR spectroscopy supported block copolymerization with neither homopolymer formation nor side reaction, e.g. transesterification. The *Pt*BMA blocks were quantitatively hydrolyzed into polyacid with formation of polyacid polyether block copolymers as supported by titration, NMR and IR analysis.

In recent years, macroinitiator and redox initiating systems have been successfully used for the synthesis of block copolymers via a radical mechanism.

Cakmak [70] used the redox polymerization of MMA using Ce^{4+} or Mn^{2+} and prepolymer containing PEO, azo and OH groups as initiator to yield MMA–EO block copolymers with labile azo linkages in the main chains (Scheme 20). These prepolymers were used to initiate the radical polymerization of MMA through the thermal decomposition of the azo groups, resulting in the formation of triblock copolymers. Successful blocking was confirmed by fractional precipitation and the molecular weight distribution.

Nagai and Terada [71] used a macroinitiator, which was obtained by condensation of azobiscyanopentanoyl dichloride with PEO monoethyl ether to initiate radical polymerization of MMA.



Scheme 21.

HO-(CH₂CH₂O)_n-H
$$\xrightarrow{CS_2+NaOH}$$

NaSSCO-(CH₂CH₂O)_n-CSSNa $\xrightarrow{H_2SO_4}$ \bullet SSCO(CH₂CH₂O)_nCS₂ \bullet $\xrightarrow{-CS_2}$
 \bullet OCH₂CH₂O(CH₂CH₂O)_{n-2}CH₂CH₂O \bullet \bullet CHCH₂O(CH₂CH₂O)_{n-2}CH₂CH₂O
OH OH

Scheme 22.

Ueda and Nagai [72] studied further this process for deriving block copolymer of PEO, which involves chain extension of PEG by polycondensation with azobiscyanopentanoic acid in the first step and decomposition of -N=N- units of the macroazoinitiator in the presence of vinyl momoners in the second step. Different monomers such as styrene, MMA, MA, vinylacetate and acrylonitrile(AN) were studied and compared. Polymerization was carried out at 60°C for 24 h, so that all the azo units completed the decomposition. Monomers having a higher overall rate of polymerization showed higher conversion as well as higher molecular weight at the same concentration of azo initiator species within the same time of polymerization. Among the vinyl monomers, methyl acrylate (MA) and MMA showed the highest conversion up to 80%–85%, whereas conversion of styrene was as low as 20%. GPC curves showed that PMA–PEO and PMMA–PEO exhibited higher molecular weight than the other monomers.

In order to synthesize a PEO–PMMA block copolymer, Yuruk and Ulupinar [73] prepared macroazocarbamate by capping OH-terminated PEO with isophorone diisocyanate and subsequently reacting this intermediate with 4,4-azobis(4-cyano-1-pentanol). The resulting polymeric azocarbamates were used as free radical initiators for the polymerization of MMA. Copolymers with $M_w = 2-7 \times 10^5$ were obtained (Scheme 21).

Cakmak [74] synthesized triblock copolymer, PMMA–PEO–PMMA, through redox initiated free radical polymerization of MMA with PEG using Mn^{2+} . The principal parameters affecting the synthesis were examined. The block copolymers were characterized by ¹H NMR and IR spectroscopy. He also prepared block copolymers of MMA and EO by polymerization of MMA using H₂O₂ and xanthate terminated PEO as redox initiator in the presence of H₂SO₄ [75] (Scheme 22).

Pascal et al. [76] prepared multiblock copolymer of PEO and PMMA from dixanthogen linked PEO and PMMA prepolymer sequences using free radicals, utilizing the high chain transfer and termination properties of dixanthogen. A simple and efficient method was developed for the synthesis of dixanthogen linked polymers: hydroxyl functionalized prepolymers (P) were reduced using NaH to form alkoxide; carbon disulfide was then added to the alkoxide to form the dixanthogen (Scheme 23).

DSC and small angle X-ray scattering investigations were reported for block copolymers of the immiscible PEO-poly(*t*-butyl acrylate) (PtBA) system in order to describe the sequences and comment

HO-P-OH
$$\xrightarrow{2\text{NaH}}$$
NaO-P-ONa $\xrightarrow{2\text{CS}_2}$ Na⁺SSCOPOCSS Na
 $\xrightarrow{[O]}$ -(S₂CO-P-OCS₂)_n-

Scheme 23.





on the morphological phase behavior [77]. Lamellar thickness is correlated with the polymerization degree of PEO and the amorphous PtBA for both the thermodynamic equilibrium and nonequilibrium methods. Nonequilibrium results differ from those of extrapolated equilibrium results, but within the experimental standard deviations the theoretical prediction for the equillibrium method could be confirmed, The knowledge of the thermal behavior gives an additional tool in block copolymer characterization.

5. Graft copolymers from the ethylene oxide and alkyl (meth)acrylate

A number of graft copolymers of alkyl (meth)acrylate with EO were synthesized by the use of basecatalyzed transesterification reaction of acrylate or methacrylate polymer with α -hydroxy- ω -methoxypolyoxyethylene of various molecular weights as in Scheme 24 [78].

Xie et al. [56,57] prepared three types of graft copolymers with uniform PEO grafts via copolymerization of PEO macromer with MMA, MA or *n*-butyl acrylate (BA) in benzene solution using AIBN as initiator. The grafting efficiency can reach about 90%. The graft copolymers were purified by extractions and characterized by GPC, IR and membrane osmometry. The average grafting number of the copolymers varied from 10 to 15. The grafting efficiency decreased with increasing macromer/monomer ratio and increased with polymerization time. They also studied the crystalline properties, emulsifying properties and phase transfer catalytic effects in the Williamson reaction for three types of graft copolymers with different backbones [56].The crystallinity decreases in the order: PS-g-PEO >PMMA-g-PEO > PMA-g-PEO. Crystallinity increases with both content and molecular weight of PEO grafts, but diminishes after complexing with LiClO₄. Both emulsifying ability and phase transfer catalytic efficiency of the copolymers decrease in the order: PMMA-g-PEO > PMA-g-PEO > PS-g-PEO. Both the emulsifying volume and the conversion in the Williamson reaction increase with amount of PEO content of the copolymer used, but decrease with increasing molecular weight of the PEO grafts.

Akashi et al. [79] indicated that polymerization of methacrylate terminated PEG with MMA proceeded homogeneously in benzene but heterogeneously in ethanol-water with the formation of microspheres. The rate of polymerization in ethanol-water was faster than that in benzene. Graft copolymers prepared in ethanol-water had a low molecular weight fraction because of soluble PEO rich copolymers and a high molecular weight fraction owing to the microspheres. Graft copolymers prepared in benzene exhibited only one GPC peak.

Xie and his coworkers [80] also synthesized (*n*-butyl acrylate (BA)–acrylic acid) copolymers with uniform PEO side chains by terpolymerization of BA and acrylic acid (AA) with PEO macromer and showed that the methacrylate terminated PEO macromers copolymerized more quickly than BA or AA at the beginning of terpolymerization. Conversion of the macromers increases with the decrease of



Scheme 25.

molecular weight of the macromer or ratio of the macromer to monomers in the feed. The IR spectrum of the purified terpolymer shows the presence of hydrogen bonds between PEO chains and PAA units. The average number of PEO side chains per molecule ranged from 6 to 16. The terpolymers can emulsifying the benzene/water system and show high water absorbency. The terpolymers exhibit crystallinity which diminishes with the increase of AA content. Tensile strength of the terpolymers increases more noticeably with AA content than with PEO content. The terpolymer was neutralized with methanolic alkali or metallic acetate at 50°C to form ionomer. IR spectrum of the ionomer indicated the disappearance of hydrogen bonds and the appearance of carboxylate groups. The strength of a terpolymer is raised markedly, when it is converted into an ionomer. The tensile strength of an ionomer containing Na⁺ or K⁺ is much lower than that for an ionomer containing divalent cations because of the stronger complex formation between PEO and univalent cations.

Xie and Liu [81] reported a chemical valve formed by poly(ethyl acrylate) with uniform PEO side chains (PEA-g-PEO) and polyacrylic acid with uniform PS side chains (PAA-g-PS). Both copolymers were synthesized by macromer technique. As poly(acrylic acid) can form a complex with PEO through hydrogen bonding between COOH groups of the former and CH₂CH₂O of the latter, the two graft copolymers can form an intermolecular complex. When a membrane made by casting a solution of PEA-g-PEO and PAA-g-PS at a molar ratio of PAA/PEO = 1 was set in the ultrafiltration cell assembly, the permeation rate of water through the membrane depends largely on pH. The permeation rate was very low at pH 10 and increased gradually from pH 9 to pH 4 and then quickly at pH 3.5. This kind of membrane formed from the complex of the two graft copolymers seems to have a physically crosslinked semi-IPN structure. The PS side chains of PAA-g-PS can form glassy domains acting as physical crosslinks in the blend, while PEO of PEA-g-PEO complexed with PAA of PAA-g-PS leaves channels in the membrane at pH about 3.5. Dissociation of the complex because of deprotonation of PAA at higher pH causes the membrane to swell, closing the channels. This membrane functions as a chemical valve because its permeability can be controlled reversibly by adjusting the chemical environment, namely the pH. The IR spectrum of the complex membrane showed a wide absorption peak at about 3100 cm⁻¹, demonstrating the formation of hydrogen bonds between COOH and CH₂CH₂O. At the same time, the absorption peak of the carbonyl group broadens and shifts to a lower wavenumber because of hydrogen bonds (at $1750-1700 \text{ cm}^{-1}$).

Wesslen et al. [82] also prepared amphiphilic graft copolymers by radical solution polymerization of methacrylate-terminated PEO macromer and acrylate or methacrylate comonomers. Most of the copolymers gave oil-in-water type emulsions at room temperature. Values for the critical micelle concentrations determined by the surface balance method were of the order of 0.1–1.5 g/l. Surface tensions of 36–56 dyne/cm were measured.

Oliveina and Lucas [83] prepared graft copolymers of MMA with diblock copolymers of ethylene oxide and propylene oxide P(EO–PO) as side chains by radical copolymerization of MMA with P(EO–PO) macromers which were synthesized by reaction of EO–PO diblock copolymer with methacryloyl chloride. The graft copolymers were characterized by GPC, VPO, IR and ¹H NMR spectroscopy. Instead of diblock copolymer of EO and PO as grafts, Amori and Oliveina [84] synthesized bigraft copolymers by radical copolymerization of two macromers (PEO methacrylate and PPO methacrylate) with MMA. The copolymers obtained contained both PEO grafts and PPO grafts.

Epoxy groups within glycidyl methacrylate copolymers were also utilized for grafting [85] (Scheme 25). The graft copolymers were surface active and could be used as emulsifiers for the preparation of stable oil-in-water and water-in-oil emulsions. Polymers containing bulky hydrophobic substituents (*t*-butyl,2-ethylhexy,phenyl)in the main straight chain are better emulsifiers than those containing small or straight chain substituents. All graft copolymers were shown to be surface active with a critical micelle concentration near 1.5 g/l and surface tension of 38–45 dyne/cm.

Lucas et al. [86] indicated that PMMA–g-P(PO–EO) and PMMA–g-P(EO–PO) comprising chemically dissimilar sequences exhibit intramolecular phase separation. These copolymers have applications in coatings and as surface tension modifiers. Two T_g s were observed, caused by the partial incompatibility of the copolymers. The activation energy of the T_g relaxation process of the main chain is decreased by the graft chain. Thermogravimetric analysis showed that pyrolysis of the graft copolymers occurs in three stages and begins on the graft chain and at a lower temperature than the pyrolysis of pure PMMA. Both the phase behavior and the thermal stability depend on the composition of the copolymers.

Liang et al. [87] studied the effect of adsorption of macromolecular surfactants with PMMA backbone and PEO side chains on the stability and rheological properties of latex dispersions using adsorption isotherms and rheological measurements. Two latex particles with diameters of 427 and 869 nm were used. The amount of adsorbed surfactants per unit area was approximately constant for both latex particles. The adsorbed amount increased with the increase of temperature as a result of reduction of solvency of the medium for the chains. The steric interaction of the particles at saturation adsorption of macromolecular surfactants was investigated using steady state stress-shear rate and oscillation measurements. The adsorbed layer thickness of surfactants on the latex particles was determined as a function of volume fraction of the dispersion.

Comb polymers with methacrylate units as backbone and PEO as side chains were synthesized by Bannister et al. [88] and Kobayashi et al. [89]. The former polymerized methoxypoly(ethylene glycol) monomethacrylate (MEO_n) in water at 0°C under nitrogen using the redox pair K₂S₂O₈/FeSO₄ for 20 min. The viscosity ranged from 0.6–1.26 (100 dl/g) in water. The comb polymer from MEO₉ shows no sign of crystallinity, whereas the side groups of MEO₂₂ are believed to crystallize. Addition of a Li salt causes a large decrease in rate of crystallization. Ionic conductivity values for LiSO₃CF₃ complexes with these two comb polymers were determined and values as high as 2×10^{-5} S/cm at 20°C were achieved, which are approximately two orders of magnitude higher than those for the PEO–LiSO₃CF₃ complex.

Kobayashi et al. [89] reported that MEO_n (n = 3,7,12 or 17) was first complexed with LiClO₄ or LiPF₆ in methanol and then polymerized spontaneously during evacuation at 60°C–80°C. The polymeric solid electrolyte with n = 7 showed an ac conductivity as high as 2.2×10^{-5} S/cm at 25°C when the weight ratio of PMEO_n/LiClO₄ is 70/30. In the case of PMEO₇/LiPF₆, 1×10^{-5} S/cm was reached, when PMEO₇/LiPF₆ = 80/20–60/40 w/w. The temperature dependence of ionic conductivity followed an Arrhenius-type plot.

6. Block and graft copolymers from EO and diene or other vinyl monomers

6.1. Block and graft copolymers from EO and diene

Block copolymers of diene and EO, e.g. polydiene–PEO and PEO–polydiene–PEO can be obtained by sequential anionic polymerization of diene and EO using monofunctional and difunctional organopotassium initiator, respectively [24]. For polymerization of EO, organolithium initiator is not effective, while the activity of organosodium initiator is lower than that of organopotassium initiator [6].

Gervais and Gallot [90] synthesized diblock copolymers of butadiene (B) and EO, PB–PEO, by successive polymerizations of B and EO in THF using cumylpotassium as catalyst and characterized the products with GPC and osmometry.

Rahman and Avny [91] made different types of block copolymers, namely, PB-PEO, PB-PEO-PB, PEO-PB-PEO, via coupling of hydroxyl-terminated polybutadiene and PEG with 2,4-toluene diisocyanate (TDI) in different molar ratios of (PB + PEG)/TDI and with different charging orders. Unreacted PEG was removed by extraction of the crude polymer with water and unreacted hydroxylterminated polybutadiene with n-hexane. Rahman and Avny [92] also prepared block copolymers from carboxyl-terminated polybutadiene and PEG either by esterification of equimolar amounts of the preformed carboxyl-terminated polybutadiene and PEG or by coupling of these prepolymers with TDI. Under the direct esterification conditions used, the ratio of PEO/PB in the block copolymers indicated the formation of block copolymers containing more of the PB segments. Crosslinking of the carboxyl-terminated polybutadiene also took place. In the presence of p-toluenesulfonic acid, 66% of the carboxyl-terminated polybutadiene and 34% of the PEO were incorporated in the soluble block copolymer leading to PB-PEO-PB. Esterification failed to lead to quantitative conversion of the preformed polymers into the corresponding block copolymer. However, PEG, carboxyl-terminated polybutadiene and TDI reacted in THF at room temperature with better conversion than the esterification method. No crosslinking occurred. Conversion of PEG was higher than that of carboxyl-terminated polybutadiene. An increase in molecular weight of the PEG led to decrease in its conversion. As the OH groups of the PEG are more reactive than the terminal COOH groups of carboxyl-terminated polybutadiene, the extent of chain extension with PEG is higher. The block copolymers showed tensile strength of 2.1-0.8 MPa with elongation at 26%-58%. An increase in PEO content or in molecular weight of PEO segments led to increase in water absorption of the copolymer.

Guo, Xie et al. [93] synthesized multiblock copolymers of butadiene and oxyethylene via a coupling reaction of α, ω -dihydroxyl polybutadiene and PEG with TDI. The product was purified by successive extractions with petroleum ether and with 20% ethanol to remove homopolybutadiene and homopolyoxyethylene, respectively. The PEO content of the purified copolymer was determined by elemental analysis and the structural parameters were calculated from number-average molecular weights of the purified copolymer, determined by membrane osmometer, and those of the dihydroxyl polybutadiene and PEG, determined by VPO. The total number of blocks varied from 60 to 100. TEM showed a multiphase copolymer. WAXD indicated that the crystallinity increased from 0% to 50% with increasing weight ratio of PEO/PB. These multiblock copolymers exhibit excellent emulsifying properties, as compared to multiblock copolymers of PEO with PS or poly(alkyl acrylate). Only 0.1 g copolymer was needed to make 100 ml water/toluene (90/10) mixture to form emulsion completely. When the weight ratio of water/toluene was changed from 90/10 to 70/30 or molecular weight of PEG was changed from 6000 to 2000, oil-in-water type emulsion was changed to water-in-oil type. The copolymers also



Scheme 26.

showed good phase transfer catalytic effect in the Williamson reaction. Conversion of potassium phenolate into butyl phenolate reached over 95% when the multiblock copolymer containing 3 mmol PEO was used for 1 g potassium phenolate, whereas no reaction occurred without using the multiblock copolymer at 90°C.

The lamellar crystalline structure exhibited by a block copolymer of PB–PEO in the presence of a preferential solvent for one block (xylene for PB and acetic acid for PEO) was studied by Gervais and Gallot [90] via X-ray diffraction and DSC. The systems of the copolymer/preferential solvent of one block exhibit two mesophases in terms of solvent concentration and temperature. In systems of the block copolymer/preferential solvent of PEO, the lamellar structure with crystallized PEO chains exists at temperature below about 45°C and at solvent concentration ranging from 0 to a value characteristic of the copolymer. In the lamellar structure the chains of PEO crystallize in two layers; the solvent forms a third layer located between the PEO layers. In system of the copolymer/preferential solvent of PB, the lamellar structure with crystallized PEO chains appears at temperatures below about 50°C and for all solvent concentrations where the mesophase exists. In the latter structure the chains of PEO crystallize, folding in two superimposed layers.

Weber et al. [94] carried out a grafting reaction of 1,2,4-triazoline-3,5-dione-terminated PEO onto polybutadiene at room temperature in THF/CH₂Cl₂. The 1,2,4-triazoline-3,5-dione group reacts rapidly and quantitatively with double bonds having allylic hydrogens. The molecular weight distribution of the graft copolymer, PB–g-PEO, was very broad, probably owing to formation of aggregates by hydrogen bonding or to micellization and reverse gelation. T_g occurred at -95° C and -60° C, corresponding to the PB and the amorphous PEO phases, respectively. The melting point of the crystalline polyether shifted to higher temperatures, as the degree of grafting increased.

Amphiphilic graft copolymers with a polybutadiene backbone and PEO side chains were synthesized by grafting NCO-terminated PEO onto partially hydroxylated polybutadiene [95] (Scheme 26). The graft copolymers were water soluble if the fraction of PEO exceeds 50 wt.%. Solutions of graft copolymers in water and THF were studied by static light scattering and viscosity measurements. The results showed that the graft copolymers formed clusters in THF solution.

Triblock copolymers of EO and isoprene (I), PEO–PI-PEO, were prepared by sequential anionic polymerization with potassium naphthalene as initiator and THF as solvent [96]. In the first step the isoprene monomer was polymerized at -40° C for 6 h. In the second step EO monomer was added to the difunctional poly(isoprenylpotassium) solution and polymerized at 25°C for 3 days. Complexation of the PEO–PI–PEO block copolymers with NaSCN changed the thermal and mechanical properties. It was shown that complexation, which occurs selectively with the PEO end blocks, can yield a semicrystalline thermoplastic elastomer that melts at about 177°C. The main characteristics of the complexed block



H(OCH2CH2)nOH PIB-PEO PIB



copolymer are a crystalline temperature, which occurs 90°C lower than that of complexed homopolymer, and good dimensional stability at high temperature. However, the tensile strength of the complexed material appears to be considerably reduced with increasing temperature. A pronounced supercooling was also observed for the uncomplexed PEO–PI–PEO block copolymer. This phenomenon seems to be a general feature of two phase block copolymers in which the crystallizable component is finely dispersed into isolated microdomains.

Morgan et al [97]. reported that a PEO–PI–PEO triblock copolymer in water formed micelles and in chloroform remained as unimers. In chloroform the copolymers exhibit floatation behavior under the influence of a centrifugal field and the polydispersity of the unimers is of quasicontinuous type rather than of a discrete type with a weight-average molecular weight of 35 000 \pm 2000. The unimers exhibit a compact conformation. The apparent weight-average molecular weight of the micelles in water is 15.0 × 10⁶, suggesting a unimer association number of 400 and a weight-average hydrodynamic radius of 42 \pm 3 nm for the micelles. Rolland et al. [98] described the formation of discrete micelles (about 0.1 µm) for the same type triblock copolymers in water and an efficient labeling of the micelles by polymerization of ¹⁴C-labelled styrene within the hydrophobic core. These micellar nanoparticles are considered as promising materials for controlled release and/or site-specific drug delivery systems. In experimental animals the micelles remained in circulation with a half-life in excess of 50 h. The results demonstrated the advantages of using block copolymers for the preparation of perfect bio-compatible surfaces such as are required for well-tolerated, long circulating particulate drug carriers.

6.2. Block and graft copolymers from EO and other vinyl monomers

Block or graft copolymers of EO and other vinyl monomers, including isobutylene and vinyl pyridine, have been synthesized by different methods and their properties studied.

Block copolymers of EO and isobutylene (IB) of the type of PIB–PEO–PIB were synthesized by Rooney [99] via coupling of phenol-terminated polyisobutylene (PIB) with hydroxyl terminated PEG through a diisocyanate (Scheme 27). The phenol-terminated PIB was obtained by polymerization of IB with *sec*-butyl phenol and SnCl₄ at -50° C. The product had a number-average molecular weight of 1000 and a functionality of 0.5 per molecule.

Diblock and triblock copolymers, PIB–PEO and PEO–PIB–PEO were prepared by Kennedy [100] from linear PIB, carrying one or two *p*-phenol terminal groups. The procedure consisted of isocyanate capping of the PIB, followed by coupling with MPEG carrying one terminal OH group. TDI gives end capping and no extension probably because of the dissimilar reactivities of the NCO groups in this molecule. By the use of PIB–C₆H₄OH, PIB–PEO diblock copolymers were obtained, whereas with HOC₆H₄–PIB–C₆H₄OH, the final products were PEO–PIB–PEO triblock copolymers. Blocking



efficiency was at least 75%–85%. DSC showed a low T_g at -70° C, associated with the PIB moiety and a melting point at 53°C, indicating the presence of crystalline PEO blocks. A block copolymer, comprising of a PIB block of $M_n = 12\ 000$ and a PEO block of $M_n = 5000$ exhibited a critical micelle concentration of 3.0×10^{-5} mol/l. The block copolymers exhibit a characteristic discontinuous behavior of intrinsic viscosities, which increase with increasing temperature in the 25°C–30°C and 35°C–45°C range but,decrease between 30°C–35°C.

Wondraczek and Kennedy [101] prepared multiblock copolymers of PIB and PEO by reaction of PEG with novel oxycarbonyl isocyanate-terminated telechelic PIB, which was obtained by conversion of hydroxyl-terminated PIB with OCNCOCI. The latter reaction is free from side reaction and provides highly reactive isocyanate-terminated prepolymers.

Kennedy et al. [102] prepared graft copolymers of isobutylene with ethylene oxide by copolymerization of α -(*p*-phenyl glycidyl ether)- ω -chloropolyisobutylene macromer with ethylene oxide (Scheme 28). The macromer was synthesized by quantitative reaction between epichlorohydrin and *p*-hydroxyphenyl-capped polyisobutylene. The product, PEO–g-PIB, was characterized by NMR, GPC and DSC.

Lubnin and Kennedy [103] described the synthesis, characterization and select emulsification properties of T- and comb-shaped sequential copolymers comprised of PEO backbone carrying one or multiple polyisobutylene (PIB) side chains linked by acetal groups. Conditions were developed under which PIB carrying an aldehyde end group (PIB–CHO) reacted with PEO carrying one or two terminal OH groups, i.e., Me(OCH₂CH₂)_nOH and H(OCH₂CH₂)_nOH to yield Me(OCH₂CH₂)_nOCH(PIB)O(CH₂CH₂O)_nMe or H(OCH₂CH₂)_nOCH(PIB)O(CH₂CH₂O)_nH, respectively. The microarchitecture and composition of these copolymers can be influenced by the CHO/OH ratio and the molecular weight of the prepolymers. These sequential copolymers form very stable oil-in-water emulsion. The linking acetal group is resistant to hydrolysis in aqueous suspension at room temperature most likely because of steric protection afforded by the bulky water-repellent PIB blocks. However, the acetal linking groups can be rapidly cleaved by 1 N aqueous HCl at about 100° C.

Cui, Xie et al. [104] reported the synthesis of poly (2-vinylpyridine)–g-PEO using a macromer technique. 2-Vinylpyridine (2-VP) was copolymerized with PEO macromer in THF or benzene solution by using azobisisobutyronitrile as the initiator. The grafting efficiency or the conversion of macromer can reach about 56%. There are maxima value in both the grafting efficiency and molecular weight of copolymer with the increase of number-average molecular weight of the PEO macromer. At the beginning of copolymerization the conversion rate of macromer was higher than that of 2-VP, but after a certain time the conversion of macromer decreased slightly and the conversion of 2-VP exceeded that of

the PEO macromer. The crude copolymers were purified by extraction with water to remove unreacted macromer, followed by dissolution in benzene and precipitation of homopolymer of 2-VP by adding toluene. The purified graft copolymer was characterized by IR, ¹H NMR spectroscopy and membrane osmometry. The number-average molecular weights of PEO grafts and copolymers can be varied from 3000 to 9000 and from 13 000 to 65 000, respectively. The graft copolymers showed electronic conductivity after being complexed with TCNQ, ionic conductivity after being complexed with LiClO₄ and mixed conductivity with a synergistic effect after being complexed with both TCNQ and LiClO₄.

Xie et al. also studied emulsifying properties, phase transfer catalytic properties and dilute solution properties of P2VP–g-PEO [105]. The results showed that these graft copolymers can emulsify the benzene/water system and increase the conversion of potassium phenolate during the Williamson reaction of solid potassium phenolate with *n*-butyl chloride or *n*-butyl bromide. The crystallinity of the graft copolymers increases with the molecular weight and content of PEO grafts, but decreases after the graft copolymer was complexed with LiClO₄. After neutralization of 2VP units with hydrochloric acid solution, the copolymers exhibit polyelectrolyte solution properties. Intramolecular phase separation phenomenon exists in a dilute solution of the graft copolymer in benzene. TEM shows that microphase separation exists in the solid state graft copolymer.

Xie et al. [106] reported the preparation of oxymethylene-linked 2-vinyl pyridine-oxyethylene multiblock copolymers by coupling PEG and α, ω -dihydroxypoly(2-vinylpyridine) with dichloromethane using KOH powder as catalyst. α, ω -Dihydroxypoly(2-vinylpyridine) was synthesized by anionic polymerization of 2VP using α -methylnaphthyl lithium as a dianionic initiator, followed by capping with EO and terminated with methanol. The multiblock copolymer doped with LiClO₄ or/and TCNQ showed ionic, electronic and mixed (ionic-electronic) conductivities. However, in contrast to the P2VP-g-PEO/ LiClO₄/TCNQ complex, no synergistic effect in the mixed conductivity was observed. The mixed conductivity is lower than or intermediate between electronic conductivity and ionic conductivity. The optimum molar ratio of EO/Li is smaller than that for homo PEO or other PEO-containing copolymers, as also found in the LiClO₄ complexed P2VP-g-PEO. This result may be caused by the ion-dipole interactions between Li⁺ ions and the basic nitrogen of the P2VP blocks, thus consuming a part of the Li⁺ ions. The multiblock copolymers are amphiphilic and show moderate emulsifying properties, which are lost in the presence of an acid., because P2VP can be neutralized with acid. Bases have no effect on the emulsifying properties of the copolymer. The PEO-containing multiblock copolymers also exhibit the phase transfer catalytic activity in the Williamson reaction. As in the case of P2VP-g-PEO, the multiblock copolymers of 2VP and EO also show polyelectrolyte behavior in dilute solution after neutralization with HCl solution. When the concentration of neutralized copolymer is lower than 0.01 g/ml, the reduced specific viscosity and the inherent viscosity increase with decrease of solution concentration.

6.3. Block and graft copolymers from EO and other acrylic monomers

Block and graft copolymers containing PEO segments and polyacrylonitrile (PAN), polyacrylamide (PAM) or polyacrylic acid (PAA) segments have also been synthesized and their properties studied.

Early in 1965 Novitskaya and Konkin [107] prepared block copolymers of EO and AN by adding a 0.1 N solution of $Ce(NH_3)_2(SO_4)_2$ in 1 N H_2SO_4 to an aqueous solution of PEG and acrylonitrile (AN) at room temperature. The reaction time was selected so as not to exceed the induction period of homopolymerization of AN. PEG had a molecular weight of 4400. Ce⁴⁺ was used as oxidizing agent for OH





groups in PEG. During the first 20 min, the reaction rate is constant, then it diminishes considerably. During the reaction, the content of PEG in the block copolymer decreases, while that of AN increases, as does the molecular weight of the copolymer. The copolymers contained 12%-20% of PEG. An increase in the PEG content in the initial mixture results in an increase in yield and conversion of AN. When the concentration of Ce⁴⁺ used is 10 mmol/l, the number of active centers can be augmented by increasing the concentration of PEG up to 5–10 mmol/l, a further increase has only a slight effect. Initiation of the reaction occurs through splitting not the O–H bond, but the C–H bond at the end of the macromolecule, with formation of the biradicals HOCH–C HOH. The copolymer retains OH groups.

Block copolymers of PAN and PEO were made by polymerization of AN with a redox initiator made from PEG xanthate and H_2O_2 [108] (Scheme 29). However, not only triblock copolymers but also pentablock copolymers were obtained, owing to different types of chain terminations.

PAN–PEO block copolymer fibers with low surface charge were also prepared using H_2O_2 -PEG xanthate redox systems [109]. The effects of molecular weights and xanthate concentrations of PEG– xanthate on the composition of the block copolymers were determined. Block copolymers of similar chemical composition was formed in the presence of PEG–xanthate containing two xanthate groups at equal xanthate concentrations independent of the molecular weight. Increasing the molecular weight of PEG–xanthate increased the PAN segment length and decreased the block copolymer yield. The average length of these segments in the copolymer prepared with PEG xanthate containing only one xanthate group was higher than that with bifunctional PEG xanthate.

PAN–PEO block copolymers can also be prepared using a macromolecular initiator containing azo groups, which was obtained by reaction between PEG and AIBN in the presence of acid [110] (Scheme 30). AN was polymerized with the initiator in aqueous solution by heating. The yield of block copolymer, PAN–PEO, showed a maximum value of 40% at 85°C, whereas the intrinsic viscosity of the copolymer decreased with increasing polymerization temperature and time. N content decreased with increasing polymerization temperature or time. GPC characterization indicated a multimodal



Scheme 30.

distribution. The water soluble fraction contains 6%-12% PAN, whereas the water insoluble fraction contains 86%-92% PAN.

A bifunctional initiator for anionic and charge transfer polymerization using p-amino phenol as parent compound is used for synthesis of diblock copolymers of EO and AN [111]. The copolymerization is divided into two stages:first, the amino group of *p*-aminophenol was protected by benzaldehyde and then reacted with metallic K and the phenoxy anion initiated the polymerization of EO. In the second stage, the PEO prepolymer with the Schiff base end group was deprotected by acidolysis, the recovered amino group and benzophenone formed the charge transfer complex, which under UV irradation initiated the polymerization of AN (similar to Scheme 6). Successful blocking was confirmed by a strong change in the molecular weight of the prepolymer PEO and the block copolymer as well as IR, DSC and NMR. T_g of a short PAN block is higher than that of longer ones. For the short PAN block, the stretched part in the interface area may play a dominant role in the glass transition, so that its T_g increases. However, for the long PAN block, prominent PAN chains are still in the random state besides in the interface area; thus, its T_g is still very similar to the PAN homopolymer. The longer amorphous block needs more folds of the crystalline block when the length of crystalline block keeps constant, so that the thinner lamellae forms. The melting point of PEO block crystals decreases with lamellar thickness, i.e. decreases with the increase of the length of PAN blocks.

Yan et al. [112] obtained PAN–g-PEO by radical polymerization of methoxy-poly(ethylene glycol) monomethacrylate (a water-soluble macromer) (A) with AN (B) in dimethylsulfoxide solution at 60°C. The process obeys the terminal unit model($r_A = 1.35$, $r_B = 0.38$) and readily yields graft copolymers over a broad range of compositions and molecular weights ($M_w = 0.5-9.0 \times 10^5$). The reactivity ratio of a macromer of higher molecular weight was estimated to be about 0.66, a significantly larger value than those of the shorter chains and ordinary alkyl methacrylates. Light scattering measurements in DMF solution at room temperature indicated that though DMF is a poorer solvent for the PEO than for PAN and in spite of the branched structure, the apparent dimensions of the copolymers seem only slightly lower than those of PAN of the same molecular weight.

Graft copolymer of PAN and PEO, PAN–g-PEO, were also synthesized by radical copolymerization of AN and methacrylate-terminated PEO macromer in dimethylformamide [113]. The macromers were prepared by reaction of methacryloyl chloride with PEG. The effects of solution concentration, initiator concentration and AN/macromer molar ratio on the conversion, molecular weight and PEO graft content in the graft copolymerization were studied. 76% conversion can be obtained using 1.5 mol% AIBN. The copolymers were purified by reprecipitation from DMF in distilled water. Molecular weights of the graft copolymers ranged from 40 000 to 61 500. The purified graft copolymers were characterized by GPC, ¹³C NMR and Kjeldhal method.

Dicke and Heitz [114] synthesized block copolymers of acrylamide (AM) and ethylene oxide using polyazoester formed from PEG and 4,4-azobis(4-cyano-1-pentanoic acid). The polyazoester was used to initiate the polymerization of AM. The block copolymer contains homopolymer of AM. The copolymers showed surface active properties and can be used as emulsifier in emulsion polymerization.

Block copolymers of PEG with AM and MAA were synthesized by Nagarayan et al. [115] using a redox system consisting of ceric ions and PEG in aqueous acidic medium. The molecular weight of PEG in the redox system was varied to obtain a series of block copolymers with different molecular weights of PEO segments. The polymerization proceeded via macroradical generation, which was substantiated by ESR spectrosopy. This macroradical acted as a redox macroinitiator for the block copolymerization of



Scheme 31.

the vinyl monomers. The formation of these block copolymers was confirmed by fractional precipitation technique and molecular weight determination.

Water soluble graft copolymers of polyacrylamide with PEO side chains (PAM–g-PEO) were synthesized by copolymerization of acrylamide (AM) with monomethoxy PEO methacrylate macromer [116]. The macromers were synthesized by a catalytic esterification of methacrylic acid with monomethoxypoly(ethylene glycol)s with different molecular weights. The graft copolymers obtained were characterized by ¹H NMR, GPC and Ubbelohde viscometry. The rheological behavior of aqueous polymer solutions was studied with a cone and plate rheometer. The polymer solutions showed association at elevated temperature.

A new kind of water soluble polymer was obtained by L'Alloret et al. [117], via grafting PEO side chains, on a hydrosoluble backbone. As PEO is characterized by a lower critical solution temperature (LCST), a phase separation occurred on heating, For semidilute solution, the side chains associate as the temperature exceeds a critical temperature (T_{ass}), which is close to their LCST. Microdomains were formed which act like physical crosslinking units between the main chains and an increase in the aqueous solution viscosity was observed. Systems based on 2-acrylamido-2-methyl propanesulfonic acid backbone and PEO side chains were developed. The graft copolymers were synthesized by copolymerization of 2-acrylamido-2-methyl propanesulfonic acid with sodium salt of acrylic acid, using ammonium persulfate and tetramethyl ethylene diamine (TMEDA) as redox initiator, followed by reaction with α -amino, ω -methoxypoly (ethylene glycol) (Scheme 31).Fluorescence measurements indicated the formation of hydrophobic microdomains on heating in agreement with the thickening properties of the solutions.

Polymeric solid electrolytes with good cationic conductivity were prepared from the complexation of graft polymer, PAM–g-PEO, with Li methoxyoligooxyethylene sulfate and Li methoxyoligooxyethylene sulfonate [118]. The electrolytes exhibit low T_g and have almost no crystallinity. Their ionic conductivity at 25°C are over 10⁻⁵ S/cm. The number of carriers in the complex decreases while

 $-(CH_2 - CH_{2n} - (CH_2 - CH_{2n} + H_2N - CH_2CH_2 - (OCH_2CH_2)_{x} OCH_3 - (OCH_2)_{x} OCH_2 - (OCH_2)_{x} OCH_2) - (OCH_2)_{x} OCH_2 - (OCH_2)_{x} OCH_2 - (OCH_2)_{x}$

 $\begin{array}{c} ---(CH_{\overline{2}}CH)_{\overline{m}} - (CH_{\overline{2}} - CH)_{\overline{m}} \\ COOH \\ CONHCH_2CH_{\overline{2}} - (OCH_2CH_2)_x OCH_3 \end{array}$

Scheme 32.

ionic mobility increases considerably with increasing temperature. The polarization reversing method confirmed that the cationic transference values are all over 0.9. The electrolytes have single ion conduction characteristics in dc polarization.

Poly(acrylic acid)–g-poly(oxyethylene) copolymer, PAA–g-PEO, was formed by polymerization of the allyl group terminated poly(oxyethylene) macromer with acrylic acid (AA) [119]. With increasing macromer concentration in the feed, the yield of graft copolymer decreased. The yield increased with increasing $K_2S_2O_8$ catalyst up to an amount equivalent to 1.5% of AA in the feed and also increased with increasing polymerization time, but the composition remained unchanged. The solution viscosity of the graft copolymer decreased with increasing EO content.

Hourdet et al. [120] developed a thermally induced association polymer by grafting lower critical solution temperature side chains (PEO) onto a water soluble polyacrylic acid (PAA) backbone, using *N*,*N*-dicyclohexylcarbodiimide (Scheme 32). Based upon the thermodynamic properties of the pendant chains, acting as reversible crosslinkers with varying temperature, such a system exhibits a thermothickening effect. In aqueous solution, this polymer provides an enhancement of viscosity on heating, the extent of which can be controlled by polymer concentration, grafting ratio and salt concentration.

7. Conclusion

Design and synthesis of different types of block and graft copolymers from EO and S, as well as different types of block and graft copolymers from EO and alkyl (meth)acrylate (RMA), diene, other vinyl or acrylic monomers have been reviewed. Copolymers with well-defined structures are emphasized. Five types of block copolymers and two types of graft copolymers from EO and S have been successfully designed and synthesized, whereas only four types of block copolymers and one type of graft copolymer from EO and RMA, butadiene or isobutylene have been prepared.Star-shaped block copolymers of EO with other monomers except styrene and some graft copolymers, such as PEO-g-PRMA, PEO-g-PB or PIB-g-PEO, have not yet been obtained successfully till now. Some diblock copolymers, such as PS-PEO, polydiene-PEO and PtBMA-PEO and some triblock copolymers, such as PEO-PS-PEO, PEO-PtBMA-PEO and PEO-polydiene-PEO, are mainly synthesized by sequential living anionic polymerization of S (or diene or tBMA) and EO using monofunctional or difunctional organopotassium as initiator, respectively. The PS-PEO-PS or polydiene-PEO-polydiene triblock copolymers cannot be prepared via this method. Multiblock copolymers are usually prepared by condensation of telechelic prepolymers, including PEG. The graft copolymers with PEO side chains have chiefly been obtained via copolymerization of PEO macromer with other monomers. Diblock copolymers can also be synthesized via macroinitiator containing PEO or redox initiating system.

Most of the copolymers containing PEO segments have been purified by extractions or fractional

precipitation and characterized by IR, ¹H NMR, GPC, DSC, TEM etc. They showed morphologies of microphase separation, micelle formation in solution, unique surface properties and also exhibited good emulsifying properties, high water absorbency, phase transfer catalytic behavior and ionic conductivty of their metallic ion complexes etc. These properties differ somewhat according to composition and structure of the copolymers. Some block copolymers of EO and S exhibited special mesomorphic phenomena in toluene solution. The multiphase copolymers of EO and S or RMA can behave like a compatibilizer for the blend of epichlorohydrin rubber with PS, PMMA or PVC. Aqueous solution of the graft copolymer of AM or AA with PEO side chains shows the thermal induced association and thickening properties at elevated temperature, as PEO chains are characterizaed by a lower critical solution temperature and form microdomains on heating, as the temperature exceeds a critical temperature. All the aforementioned properties have promising prospects for industrial utilization.

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