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AMPHIPHILIC GRAFT COPOLYMERS — PREPARATION AND INTERFACIAL PROPERTIES

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Abstract: Amphiphilic graft copolymers containing poly(ethylene oxide) (PEO) grafts have been prepared by various methods, for example, by coupling of reactive hydrophobic backbone polymers with end-functionalised PEO, by macromonomer copolymerisation, and by anionic graft polymerisation of EO onto polymer backbones carrying functional groups as initiator precursors. The graft copolymers are amphiphilic and were shown to accumulate at surfaces and interfaces in solution and in the solid state. Amphiphilic starch derivatives were prepared by reaction of amylose and starch with aliphatic α-epoxides.

INTRODUCTION

Copolymers prepared from monomers which differ in polarity or hydrophilicity generally show surface activity and accumulate at interfaces, for example, at free surfaces or at interfaces of heterogeneous blends (Ref. 1). The amphiphilic properties become more pronounced if the difference in polarity is significant or if longer segments of the different monomer residues are present in the macromolecules. Polymers which contain strongly hydrophilic and hydrophobic groups or segments in the same molecule are genuinely amphiphilic and show an interfacial behaviour similar to that of low molecular weight amphiphiles, i.e., surface accumulation, adsorption, and aggregation (Ref. 2).

The amphiphilic polymers can be branched macromolecules composed of hydrophobic main chains carrying hydrophilic groups or grafts distributed along the chains, or *vice versa* (graft or comb polymers), or hydrophilic and hydrophobic chains coupled together to form linear polymers (block copolymers). The amphiphilic properties of the polymers depend on the balance between the hydrophilic and hydrophobic segments, i.e., the hydrophilic/hydrophobic balance (Ref. 2).

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Amphiphilic polymers can be prepared from petrochemicals as well as from renewable resources such as cellulose, starch, and other types of polysaccharides. Polysaccharides, being inherently hydrophilic, have to be derivatised by introduction of hydrophobic groups or chains in order to become amphiphilic. However, even small degrees of substitution give large effects on the solution behaviour of the polysaccharides, for example, the adsorption and association behaviour. At high degrees of substitution the derivatives behave as hydrophobic polymers soluble in organic solvents.

Because of their interfacial properties, amphiphilic polymers can be utilised in a large number of applications. Many of the applications are consequences of the adsorption and aggregation properties of the polymers in solution. For example, amphiphilic polymers are used for rheology control in foods and paints, as gel formers in pharmaceuticals, as flocculation agents and binders in papermaking and in paper coatings, as surface modifiers for fibres, etc. Amphiphilic block and graft copolymers are also used for surface and interfacial control in polymer processing and in polymer blend applications.

At our laboratories research concerning preparation and properties of different types of amphiphilic polymers have been carried out for a number of years.(Refs. 2 - 12) The aims of the research are to investigate structure/property relations for amphiphilic polymers, with particular emphasis on the behaviour of polymer solutions and polymer blends. In the present communication will be reported and discussed the preparation and properties of some different types of amphiphilic polymers based on petrochemical precursors such as styrene, acrylates, and ethylene oxide, and from biological precursors such as starch and amylose.

RESULTS AND DISCUSSION

Ethylene Oxide Graft Copolymers

Graft copolymers composed of hydrophobic main chains and hydrophilic poly(ethylene oxide) (PEO) side chains have been synthesised by various methods (Refs. 2-9). As shown in Fig. 1, graft copolymers have been prepared through coupling reactions of functional polymers such as acrylic/methacrylic copolymers (Refs. 2, 6) as well as ethylene-co-acrylic acid (Ref. 8) and maleic anhydride-co-alkyl acrylate polymers (Ref. 7), and PEO monomethyl ethers (MPEO). The coupling reactions were performed either in solution or in a melt at elevated temperature, in the presence of a catalyst. It was shown that graft densities corresponding to ten grafts per 100

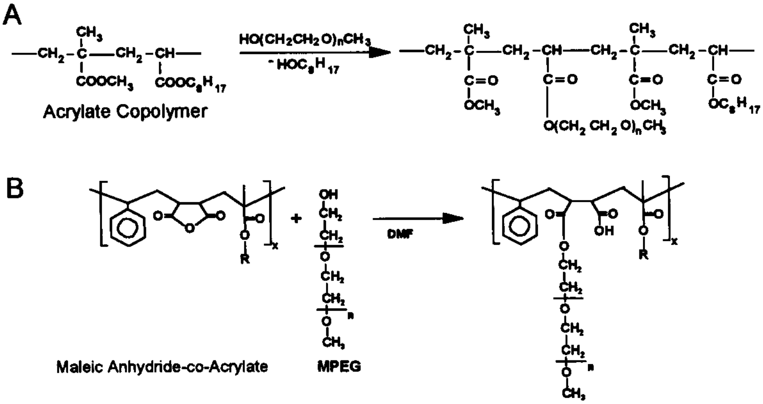

Fig. 1. Preparation of graft copolymers through A) transesterification of poly(acrylate) with PEO monomethyl ether (MPEO), and B) by ring-opening reaction of anhydride groups in a styrene/alkyl methacrylate/maleic anhydride copolymer with MPEO.

monomer units in the backbone could easily be obtained. Higher densities, however, were not readily obtainable through this method because of decreasing reactivity of the functional groups due to steric shielding.

By radical copolymerisation of MPEO macromonomers with hydrophobic acrylic monomers (Fig. 2), comb polymers similar to those described above were attainable. However, because of chain transfer to the MPEO macromonomers the reactions easily gave cross-linked gels unless the polymerisation was performed in dilute solution (Ref. 3).

Ethylene oxide (EO) is a very reactive compound and can be polymerised to PEO by anionic initiation under proper conditions. Special precautions have to be taken for handling of EO because of its reactivity and its potential carcinogenity. By using a macromolecular initiator, block and graft copolymers containing PEO grafts may be prepared. As shown in Fig. 3,

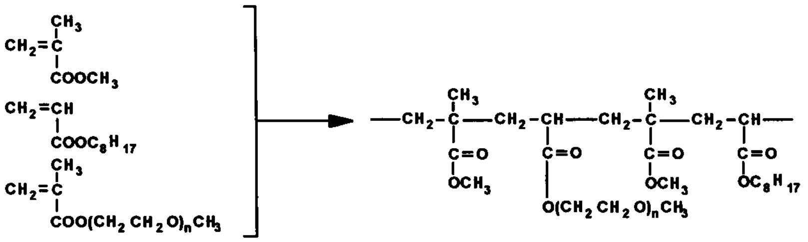

Fig. 2. Preparation of comb polymers through radical solution copolymerisation of MPEO-methacrylates with alkyl acrylates and methacrylates.

amide groups in styrene/acrylamide copolymers (Ref. 5) and in polyamide 12 (Ref. 9), were utilised as reactive sites for the EO polymerisation, and copolymers containing grafts of PEO of various molecular weights could be prepared. The polymerisations were carried out under pressure in 2-ethoxyethyl ether or in dimethyl sulfoxide. Also, ethylene-vinyl alcohol copolymers (EVOH) could readily be grafted with ethylene oxide by this method (Ref. 9). By alkylation of the living PEO chains-ends, hydrophobic alkyl groups of different lengths, or sulphonic acid groups (Ref. 10), could be introduced into the graft copolymers. The polymerisation of EO and the alkylations were performed in a pressurised calorimetric reactor which allowed close monitoring of the reactions.

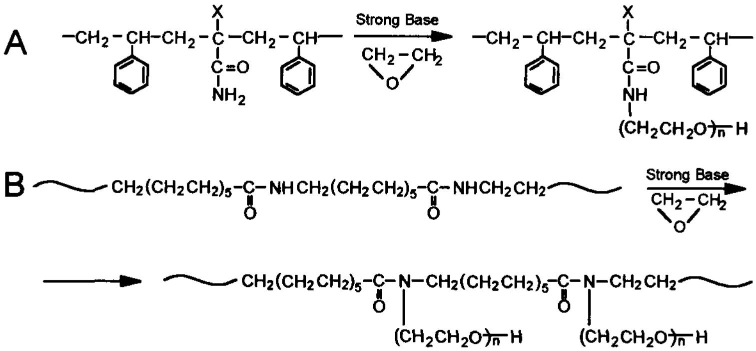

Fig. 3. Preparation of graft copolymers through ethoxylation of A) poly(styrene-co-acrylamide), and B) polyamide 12.

Amphiphilic Polymers from Starch and Amylose

Native starch is generally present in plants as semi-crystalline granules containing branched amylopectin and linear amylose. On derivatization of native starch it has to be taken into account that the constituents have different structures and reactivities and that the crystallinity of the granules may produce an uneven substitution of the two polymers. The substitution reactions can be performed under various conditions, e.g., in an aqueous slurry, in an aqueous solution, in a plasticised melt, or in a non-aqueous solution.

We have studied the preparation of amphiphilic derivatives of potato starch by a sodium hydroxide catalysed reaction with aliphatic α-epoxides, from C3 to C16, in aqueous slurry and aqueous solution (Fig. 3). Even though the intended degree of substitution (DS) was only 0.1,

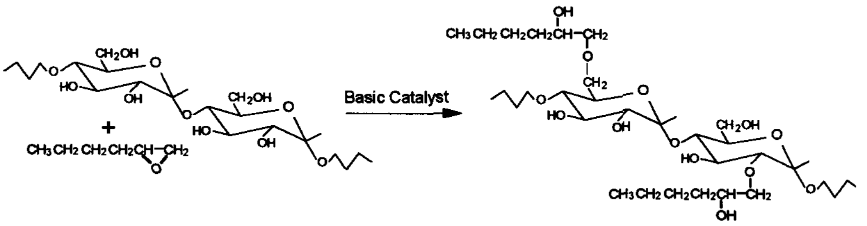

Fig. 4. Preparation of alkoxy derivatives of amylose by base-catalysed reaction with alkyl α-epoxides.

the limited solubility and the poor compatibility of the long-chain epoxides with starch gave low reaction yields, on the order of 4 - 50 %, the lower yields obtained with the C16 epoxide (Ref. 11). The association behaviour of the starch macromolecules presents a further obstacle for the derivatization. Special reaction conditions thus have to be used with the long-chain aliphatic α-epoxides in order to reach high DS value in an aqueous environment.

Starch as well as amylose dissolves readily in DMSO, presumably to give molecularly dispersed solutions. DMSO was utilised as a reaction medium for derivatization of amylose and native and degraded potato starch with aliphatic α-epoxides. The reaction yields were found to depend on time, temperature, and the type of catalyst used. With the C12 α-epoxide reaction yields of 30-60 % were obtained with sodium hydride as a catalyst, and DS values between 0.5 and 2 could readily be reached (Ref. 12).

Properties of Amphiphilic Polymers

Aqueous solutions of amphiphilic graft copolymers have low surface tensions with cmc values on the order of 0.5-1 g/L (Refs. 2, 3). However, the adsorption at hydrophobic surfaces depends on the hydrophobicity of the surface. It was shown by ESCA, AFM and ellipsometry that the graft copolymers adsorbed at hydrophobised silica surfaces (Ref. 13), while they showed no tendency to adsorb at poly(ether urethane) surfaces which were moderately hydrophobic (Ref. 14). This behaviour should be a consequence of self-association in aqueous solution, i.e., the formation of unimeric and multimeric micellar structures which have been observed by dynamic light scattering and field flow fractionation. The entropic driving force for unfolding of the self-associated backbones and adsorption of the polymer at the hydrophobic surface should be rather small, because the hydrophilic corona formed by the PEO grafts would effectively shield the hydrophobic interior of the unimers from contacts with the aqueous

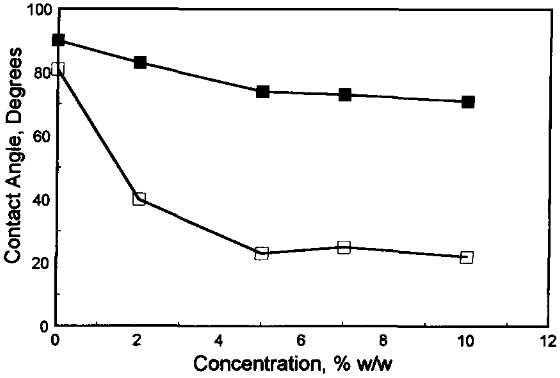

Fig. 5. Contact angles with water for a blend of polystyrene and poly(styrene-graft-PEO). Filled squares, advancing angle; open squares, receding angle.

medium. The moderately polymer surface can be expected to bind water molecules by dipolar and hydrogen bonds, and the binding enthalpy should overrun the small entropy gain connected with the adsorption process (Ref. 13).

Amphiphilic copolymers containing PEO grafts are surface active when present in polymer blends and migrate to surfaces and interfaces (Refs. 14, 15). Similarly to the situation in an aqueous solution, the polymers may phase separate when the limit of solubility in the blend has been reached, with formation of micelle-like aggregates. It was shown that poly(styrene-*graft*-EO) when present in small amounts in polystyrene, on solution casting on glass surfaces gave films with surface properties quite different from that of the original polystyrene (Fig. 5) (Ref. 16). It can be noted that in this case the backbone of the graft copolymer was compatible with the polystyrene matrix, while the grafts were incompatible. The graft copolymer was enriched at the glass/polymer interface, and at concentrations higher than 3 wt-% the surface properties remained constant, indicating that the interface was fully occupied by the graft copolymer. At this concentration a small melting transition corresponding to crystalline PEO grafts could be observed by DSC, and onion-like spherical aggregates appeared in the polymer matrix, according to transmission electron microscopy (Fig. 6) (Ref. 17). The aggregates consisted of lamellar shells of crystalline PEO grafts with a lamellae thickness of approximately 10 nm, interleaved with the amorphous polystyrene backbones.

The relative compatibility of the matrix, the backbone and the grafts, as well as the hydrophilic/hydrophobic balance of the graft copolymer, influences the surface enrichment and

Fig. 6. Transmission electron micrograph of micelle-like aggregates present in blends of polystyrene and poly(styrene-*graft*-PEO). The lamellar PEO phase domains are stained dark with ruthenium oxide.

the morphology of the polymer blend. The effects of molecular architecture of the amphiphilic polymer and the compatibility of the different polymer segments of the amphiphile with the polymer matrix are presently being studied and reported.

Amphiphilic graft copolymers present at a surface changes the surface interactions of the material with its environment, e.g., wetting, adsorption, and adhesion. For example, we have shown that surfaces modified by amphiphilic PEO graft copolymers show significantly lower adsorption of proteins, e.g., albumin, fibrinogen, and fibronectin, as compared to the original surfaces (Refs. 13, 14). The protein repellent properties are similar to those of surface-grafted PEO, which points at a participation of the PEO side-chains present in the amphiphilic polymer. However, substantially shorter PEO chains were needed with the graft copolymers to reduce the protein adsorption to similar levels. The special surface morphology obtained with the graft copolymers may thus be of significance.

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REFERENCES

(1) Y. Lyatskaya, D. Gersappe, N. A. Gross, A. Balazs, *J. Phys. Chem.* **100**, 1449 (1996).

(2) B. Wesslén K. B. Wesslén, *J Polym. Sci., A*, **27**, 3915 (1989).

(3) B. Gao, B. Wesslén, K.B. Wesslén, *J. Polymer Sci., A*, **30**, 1799 (1992).

(4) M. Kober B. Wesslén, *J. Polymer Sci., A*, **30**,1061 (1992).

(5) P. Jannasch B. Wesslén, *J. Polymer Sci., A*, **31**, 1519 (1993).

(6) L. Zhu, O. Gunnarsson B. Wesslén, *J. Polymer Sci., A.*, **33**, 1257 (1995).

(7) H. Dérand B. Wesslén, *J. Polym. Sci., A*, **33**, 571 (1995).

(8) Å. Halldén and B. Wesslén, *J. Appl. Polymer Sci.*, **60**, 2495 (1996).

(9) H. Dérand, P. Jannasch, B. Wesslén, *J. Polym. Sci. A*, to appear.

(10) H. Dérand, B. Wesslén, B.-E. Mellander, *Electrochimica Acta*, to appear.

(11) P. Gavelin, H. Werner, B. Wesslén, to be published.

(12) K. B. Wesslén, B. Wesslén, to be published.

(13) C. Freij-Larsson, T. Nylander, B. Wesslén, *Biomaterials*, 17, 2199 (1996).

(14) C. Freij-Larsson, P. Jannasch, B. Wesslén, *Biomaterials*, to appear.

(15) M. Kober and B. Wesslén, *J. Appl. Polymer Sci.*,**54**, 793(1994).

(16) P. Jannasch, B. Wesslén, unpublished results.

(17) P. Jannasch, H. Hassander, B. Wesslén, *J. Polym. Sci., B, Polym. Phys.*, **34**, 1289 (1996).