

Synthesis of New Amphiphilic Block Copolymers. Block Copolymer of Sulfonated Glycidyl Methacrylate and Alkyl Methacrylate

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Synopsis

Water-soluble amphiphilic block copolymers consisting of a hydrophobic block of poly(alkyl methacrylate) and a hydrophilic anionic polyelectrolyte block have been synthesized by a living anionic polymerization of methyl methacrylate and glycidyl methacrylate and subsequent selective modification of the oxirane groups of the glycidyl methacrylate block into hydroxysulfonate groups by a phase transfer catalyzed sulfonation reaction. The block copolymers were characterized by a predictable molecular weight and a narrow molecular weight distribution while the yield was quantitative. These amphiphilic block copolymers display surfaceactive behavior in water and they are characterized by a critical micelle concentration.

INTRODUCTION

Water-soluble amphiphilic copolymers consisting of two blocks of opposite philicity form a class of surface-active materials finding steadily increasing applications, e.g., in the biomedical field,¹ in the new technologies based on the conversion and storage of solar energy,² and in techniques requiring the stabilization of solid-in-liquid dispersions or emulsions.³ Due to the hydrophobic interactions of the nonpolar blocks, this type of copolymer can promote the formation of supermolecular "micellar" structures in water.

Anionic polymerization is undoubtedly the most appropriate method for the synthesis of block copolymers, the molecular weight and composition of which are largely controlled. However, the direct synthesis of a polyelectrolyte block is quite a problem since the related charged monomer is not susceptible to a living polymerization. Block polymerization of two uncharged monomers followed by the selective functionalization of one block should thus provide for the most successful strategy for the controlled synthesis of water-soluble amphiphilic block copolymers. This reaction pathway has been illustrated by the copolymerization of trimethylsilylmethacrylate as initiated by living polyanions of dimethylaminostyrene,^{4,5} 4-vinylpyridine,⁶ and 9-vinylphenanthrene.⁷ After hydrolysis of the trimethylsilylester groups, copolymers comprising a polymethacrylic acid block are obtained. It has however been stated that these polymerizations are not truly living processes.⁸

Amphiphilic block copolymer with anionic polyelectrolyte blocks have also been obtained by anionic polymerization of alkyl methacrylates and *t*-butyl

methacrylate⁹ or *t*-butyl acrylate¹⁰ and subsequent selective hydrolysis into a poly(meth)acrylic acid block. Recently, the anionic polymerization of glycidyl methacrylate has been found to obey a living mechanism.¹¹ Accordingly, it is quite feasible to prepare block copolymers of alkyl methacrylate and glycidyl methacrylate (GMA) and to convert the oxiranyl groups of GMA into β -hydroxysulfonate groups, thus leading to a polyelectrolyte containing copolymer.

EXPERIMENTAL

Monomers

Methyl methacrylate and glycidyl methacrylate were dried over calcium hydride under a high purity nitrogen atmosphere for several days. They were fractionally distilled from finely divided calcium hydride, and the first and last fractions were eliminated. Just before polymerization, methyl methacrylate was distilled under reduced pressure after the dropwise addition of a solution of triethylaluminum in hexane. The appearance of the greenish-yellow color, characteristic of the triethylaluminum-methacrylate complex, was the indicator of the monomer purity.¹²

Since triethylaluminum reacts fastly with the oxirane subunits of glycidyl methacrylate, removing the last traces of proton donors (such as methacrylic acid and glycidol) is questionable. It is the reason why the monomer was finally distilled from a toluene solution that contained a small amount of polystyryllithium. At room temperature, this procedure hardly promoted any polymerization of glycidyl methacrylate and the pure monomer was distilled in high yield (typically > 90%).

Initiator

s-BuLi was commercially available as a cyclohexane solution (Janssen Chimica).

Solvent

THF solvent was dried by refluxing over sodium benzophenone for several days, and distilling therefrom under a high purity nitrogen atmosphere.

Polymerization

All polymerizations were carried out in ordinary laboratory glassware. The reaction flask was put under vacuum and thoroughly flame-dried. Solvent and monomers were transferred to the polymerization flask through a stainless steel capillary. In a typical polymerization experiment, a 3000 mL Pyrex flask, fitted with a rubber septum equipped stopcock was loaded with 1500 mL of dry THF solvent. α -Methylstyrene (α -MeSt) (4 mL; 3.08×10^{-2} mol) was added to the solvent under stirring; 1.48M *s*-BuLi solution in cyclohexane was then added until the deep red color of the α -methylstyrylanion persisted. Six milliliters of 1.48M *s*-BuLi solution was then transferred into the reactor as the required initiator amount. The flask was cooled to -78°C within a dry ice-acetone mixture before methyl methacrylate (MMA) (7 mL; 6.54×10^{-2}

mol) was added. The color of the solution changed from deep red to yellow and 1 h later glycidyl methacrylate (GMA) (40 mL; 0.29 mol) was added. Approximately 20 min later, the solution was viscous and opaque, and the polymerization was terminated by addition of methanol after a 1 h period. Yield was quantitative.

Synthesis of the Amphiphilic Copolymer: Sulfonation of the Poly(Glycidyl Methacrylate) Block

Ring-opening of oxiranes as promoted by sulfite in aqueous medium leads to the formation of hydroxysulfonate derivatives.¹³ Quite interestingly, a phase transfer catalyst was used to perform the nucleophilic substitution of chloride for azide groups on polyvinylchloride in water suspension.¹⁴ Rånby et al. have also reported on the sulfonation of glycidylmethacrylate random copolymers using a phase transfer catalyst.¹⁵ These experimental conditions have been extended to the conversion of the poly(glycidyl methacrylate) moiety of the PMMA-*b*-PGMA copolymer into a polyelectrolyte block.

Typically, tetrabutylammoniumbromide (33 g; 0.1 mol) and anhydrous sodium sulfite (50 g; 0.4 mol) were dissolved in 200 mL of deionized water in a 1000 mL flask equipped with a condenser. The finely divided block copolymer (20 g PMMA-*b*-PGMA); 76 mol % of GMA) was suspended in the stirred aqueous solution, and 20 mL of chloroform were finally added. The suspension was deoxygenated with a stream of nitrogen and heated at 80°C for 30 h. After titration, 1.9 mmol SO₃⁻ g⁻¹ sulfonated block polymer were determined.

Purification of the Sulfonated (PMMA-*b*-PGMA) Block Polymer

After decantation of the aqueous solution, the chloroform swollen polymer was dissolved in deionized water and extensively purified by dialysis in Visking (24 Å) dialysis membrane bags against regularly replaced deionized water.

Measurements

GPC measurements were carried out in THF at 35°C using a Waters 200 instrument. A PMMA calibration curve allowed number and weight average molecular weights to be calculated from the elution curves.

Surface tensions were measured with a Kruss K 10 tensiometer thermostated at 20°C. The Wilhelmy plate method was used. The degree of sulfonation of the block copolymer was determined by converting the sulfonate groups into acid ones using an ion exchange resin (DOWEX 50 W) and then titrating the acid groups with standardized NaOH solution.

RESULTS AND DISCUSSION

Preparation of the (PMMA-*b*-PMGA) Copolymers

Block copolymers of methyl methacrylate and glycidyl methacrylate were prepared by using a living poly(methyl methacrylate) block as the initiator of the glycidyl methacrylate polymerization. Figure 1 shows the GPC curves of the polymer obtained (A) before and (B) after the addition of GMA. A large

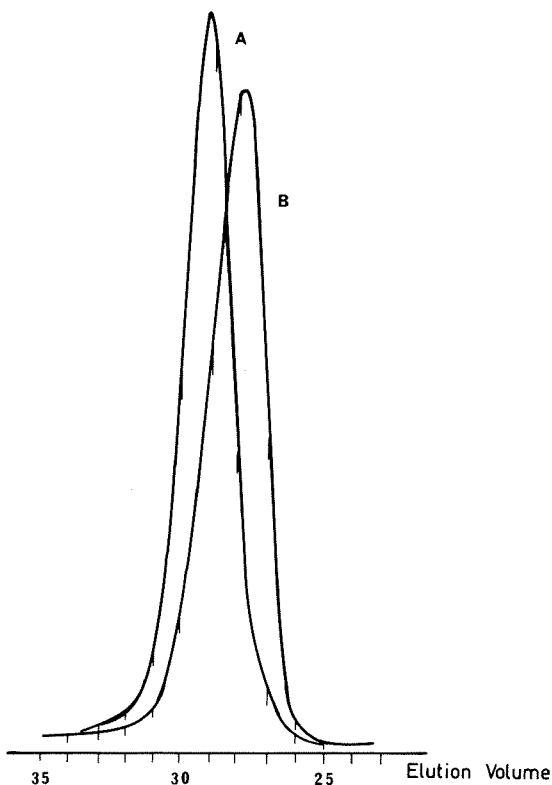


Fig. 1. GPC chromatogram of (A) L183 (see Table I) PMMA prepolymer and (B) corresponding PMMA-*b*-PGMA block copolymer.

increase in molecular weight occurs upon the addition of GMA to the living PMMA, supporting the formation of block copolymer.

In Table I, \bar{M}_n of the block copolymer was calculated from the amount of added GMA and the \bar{M}_n of the first (PMMA) block, as determined by GPC measurements. Assuming that in a truly living polymerization the molecular weight is determined by the monomer to initiator molar ratio, it can be seen that the experimental GPC determinations correspond well with the calculated \bar{M}_n of the block copolymer.

Yield of the polymerization is quantitative and the \bar{M}_w/\bar{M}_n values are smaller than 1.2.

Broadening of the molecular weight distribution of the block copolymer is observed when the initiating living PMMA block is very short compared to the PGMA block. This might be due to the moderate solubility of PGMA in THF at low temperature. In these conditions, the block copolymerization might proceed at low temperature in micelle-like structures, the more soluble PMMA block stabilizing the fine dispersion of the growing block copolymer.¹¹

When PMMA-*b*-PGMA block copolymers are dissolved in THF, opaque solutions are observed at low (-78°C) temperature. Upon increasing temperature (-10°C), THF is becoming a better solvent for both blocks and completely transparent solutions are ultimately observed. Transition from cloudy to transparent solutions depends on the relative composition and molecular

TABLE I
Anionic Block Copolymerization of (PMMA-b-PGMA)

Sample	m_{MMA}^a (g^{-1})	m_{GMA} (g^{-1})	\bar{M}_n^b PMMA _{exp}	\bar{M}_n^c (PMMA-b-PGMA) _{exp}	\bar{M}_n^d (PMMA-b-PGMA) _{calc}	\bar{M}_w/\bar{M}_n
L183	40.5	34.6	1.4×10^4	2.4×10^4	2.6×10^4	1.21
L406	8.2	40.1	2.2×10^3	1.1×10^4	1.0×10^4	1.18

^a m_{MMA} : quantity of MMA monomer added for polymerization.

^b \bar{M}_n PMMA_{exp}: \bar{M}_n of the PMMA block of the PMMA-b-PGMA copolymer as determined from the GPC chromatogram. A sample of the living PMMA was taken out before adding GMA.

^c \bar{M}_n (PMMA-b-PGMA)_{exp}: \bar{M}_n of the block copolymer as determined from the GPC chromatogram.

^d \bar{M}_n (PMMA-b-PGMA)_{calc}: theoretical \bar{M}_n of the block copolymer calculated from \bar{M}_n PMMA_{exp} and added monomer quantities.

weight of the block copolymer.¹¹ At low temperatures, block copolymers with a high PGMA content form milky white solutions, whereas these polymers with a high PMMA content generate hazy blue solutions.

The block polymerization of glycidyl methacrylate can also be initiated by other living poly(alkyl methacrylate) blocks such as polyisodecyl-, polydodecyl- and poly(2-ethylhexyl methacrylate), leading to well characterized block copolymers.

Properties of Sulfonated (PMMA-b-PGMA) Aqueous Solutions

The sulfonated block copolymers are readily solubilized in water when the hydrophobic PMMA content is smaller than 30 mol %; otherwise methanol/water or THF/water solvent mixtures are required to dissolve the amphiphilic

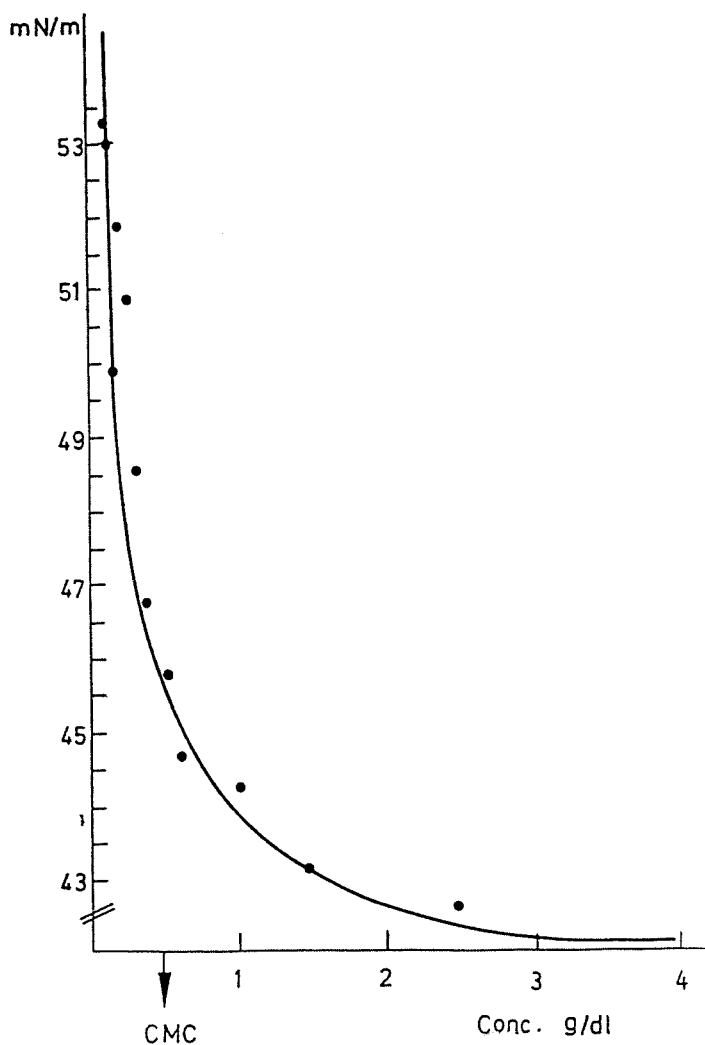


Fig. 2. Plot of the surface tension versus concentration of sulfonated PMMA-b-PGMA (L406) in water.

block copolymers. Water-soluble amphiphilic polymers are expected to form hydrophobic domains in water, due to the possible hydrophobic interaction of the nonpolar component.¹ Thus, as for low molecular weight surfactants a critical micelle concentration (CMC) should characterize the solution behavior of the amphiphile diblocks under investigation. Accordingly, Figure 2 shows that the surface tension of the sulfonated block copolymer L 406 (see Table I) decreases dramatically upon increasing concentration in water; above ca. 2 g dl⁻¹, the surface tension does not change anymore. This behavior suggests the formation of polymolecular micelles at a concentration of 0.5 g dl⁻¹. That the surface tension levels off at concentrations greater than these exhibited by low molecular weight surfactants is supported by polyether containing block copolymers.³

The cross section of macromolecules at the liquid-air interface can be determined from the slope of the surface tension versus concentration curve. The surface tension of the sulfonated PMMA-*b*-PGMA aqueous solutions were not very reproducible when measured by the Du Nouy ring method (i.e., under nonequilibrium conditions¹⁶), while the Wilhelmy plate method was poorly accurate, especially in the low concentration range. In these conditions, any comment about information of the block copolymer at the interface is subject to criticism. It is the reason why fluorescence and light scattering measurements will be undertaken in the near future.^{17,18}

CONCLUSIONS

A new family of water-soluble amphiphilic block copolymers is now available thanks to the living anionic polymerization of alkyl methacrylates and glycidyl methacrylate, followed by sulfonation of the poly(glycidyl methacrylate) block. Composition and molecular weight are predictable while the MW distribution is narrow. The sulfonated block copolymers display surface activity in water and formation of polymolecular micelles was indicated by a CMC at fairly high surface tension.

Potentialities of these products as polymeric surfactants in the preparation and stabilization of polymer latices in aqueous medium are currently investigated and will be the topic of forthcoming papers.

The authors are most grateful to the Institut pour la Recherche Scientifique dans l'Industrie et l'Agriculture and to Agfa-Gevaert N.V. for financial and scientific support. Dr. W. De Winter and Mr. N. C. de Jaeger from Agfa Gevaert R & D Labs are especially thanked for many stimulating discussions. They also want to thank Mrs. A. Fonzé and Miss G. Peiti for skillful technical assistance.

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Received August 22, 1988

Accepted June 27, 1989