Novel Amphiphilic Block Copolymers by Polymer Reactions and Their Use for Solubilization of Metal Salts and Metal Colloids

Markus Antonietti,* Stephan Förster, Jürgen Hartmann, and Sascha Oestreich

Max Planck Institut für Kolloid- & Grenzflächenforschung, Kantstrasse 55, D-14513 Teltow-Seehof, Germany

Received September 26, 1995; Revised Manuscript Received January 30, 1996[⊗]

ABSTRACT: A variety of amphiphilic blockcopolymers (ABC's) are made by using two highly effective polymer analogous reactions, epoxidation followed by opening of the oxirane ring. The optimization of all reaction conditions results in functional polymers which are practically as narrowly distributed as their precursor polymers, and which can be used as model polymers. In case of polar modification, all amphiphilic block copolymers form well-defined micelles in toluene, the size of which can be adjusted by the type of modification. The adjustment of the amphiphilicity with diverse nitrogen, sulfur, and phosphonate derivatives results in polymeric amphiphiles with a high affinity to transition metal ions, as well as metal colloids and surfaces. This is demonstrated by solubilization of metal salts in unpolar solvents by the ABC's and subsequent formation of well-defined noble metal colloids which are—in the case of a careful adaption of the polymer to the metal surface—perfectly stabilized by the corona polymers.

I. Introduction

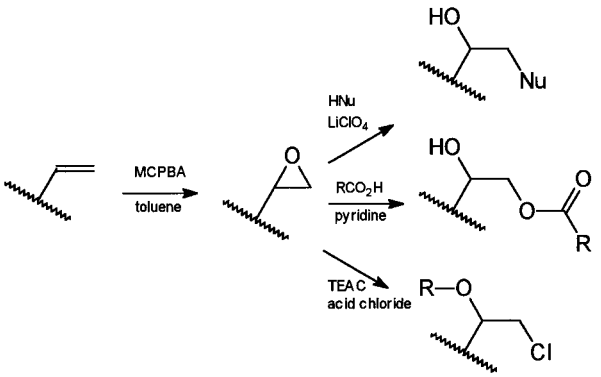
The synthesis of amphiphilic block and graft copolymers and the characterization of their properties are very current topics of research, driven by technological demands and the requirements of the society. For instance, these polymers are discussed as candidates to substitute surfactant molecules in heterophase stabilization problems, as in emulsion polymerization or for the formulation of cosmetics and drugs. The advantages of polymers are obvious: as high molecular weight components, their critical micelle concentration can be controlled to be extremely low, so that they keep their efficiency even at high dilution. Related to this, a washing out and a release to the environment is made more difficult. For some technological applications, it is interesting to mention that also the kinetic stability of the aggregation structures is easily adjusted by chemistry and block length: as compared to the millisecond region of low molecular weight surfactants, the lifetime of block copolymer micelles can easily be adjusted to be in the the second, minute, or hour region.

From a chemist's point of view, the most prominent advantage of amphiphilic polymers is the wide variability of the chemical structure of the polymer: by choice of the repeat unit, a possible copolymerization, the length and the structure of both polymer parts, we are able to adjust our molecules very specific to the demands and doubtless in a much wider range compared to low molecular weight surfactants.

Particularly with amphiphilic block copolymers, it is possible to speculate about a "generalization of amphiphilicity", i.e., to design molecules which stabilize not only the oil−water interface (the classical problem of amphiphiles), but any interface between different materials with different cohesion energies or surface tensions. In this context, we must remember that compatibilization of polymer blends or stabilization of filler particles or dye pigments can also be expressed as a problem of surface stabilization. The objective of an adjustable "amphiphilicity", however, requires a careful choice of both the solvating as well as the binding block of the ABC molecule.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

Scheme 1



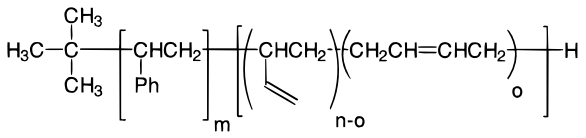
The current approaches to the synthesis of ABC's usually require "living" polymerization techniques, such as anionic,[1] cationic,[2] or group transfer polymerization.[3] In the case of two polymerizable comonomers, the block copolymers may be synthesized directly; in the case of one component which cannot be polymerized according to a living mechanism, macromonomer synthesis[4,5] or the capping with special end groups for restarting, chain transfer, or termination[6,7] is also possible. In most cases, high purity during the reactions, tedious isolation procedures, or/and the use of protecting group chemistry is required. This makes ABC's, aside from a few exceptions such as poly(ethylene oxide)-*b*-poly(propylene oxide), very expensive and prohibits many technological applications.

In the present paper, we want to make use of an alternative route to these molecules: a block copolymer which is comparably cheap and easily accessible, i.e. polystyrene-*b*-polybutadiene, is transferred via a two-step reaction into a class of new amphiphilic polymers, as shown in Scheme 1.

For the first step, we choose the epoxidation reaction of the double bonds of the polybutadiene block. It is known from the literature that some simple epoxidation agents can be used where close-to-complete conversion at a tolerable amount of side reactions, such as cross-linking, are to be expected.

Following the epoxidation, a variety of opening reactions of the oxirane ring, such as the nucleophilic (Nu

S0024-9297(95)01446-X CCC: $12.00



(PSB-I: m≈435, n≈109 ; PSB-II: m≈423, n≈390; o≈n·30%)

Figure 1. Structures of the polymers used for amphiphilic modification. For PSB-I, $m = 435$ and $n = 109$; for PSB-II, $m = 423$ and $n = 390$. In both cases, the 1,4-content o is about $o = 0.3$ n.

= nucleophile) ring opening and the reaction with acid chlorides, are applied to introduce a wide variety of different functional side groups via simple low molecular weight reactants. The central topic of the present publication is the amphiphilic functionalization reactions on metal complexing side groups, thus resulting in lipophilic/metalophilic block copolymers.

Accompanying all steps, the quality of the polymers is checked with NMR and GPC (whenever possible) to ensure uniform and well-defined products.

The amphiphilicity of all polymers is visualized by the ability to form micelles at first. This is tested with dynamic light scattering, thus resulting in a hydrodynamic radius and its distribution. A second test is the solubilization of diverse transition metal salts in these micellar solutions which are otherwise insoluble in toluene. Using these metal salt containing micelles as "molecular reactors", the usefulness of the high kinetic and thermodynamic stability of polymeric surfactant micelles is demonstrated by the model reaction of transferring the metal salts to metal colloids of uniform size in the nanometer region, following a very actual route being currently developed and optimized in a number of research groups.[8−14]

II. Experimental Section

II.1. Polymer Synthesis. The synthesis of polystyrene-*b*-polybutadiene block copolymers via anionic polymerization and their characterization were performed as described in earlier publications.[15]

The present work was restricted to only two different, narrowly distributed polystyrene-*b*-polybutadiene copolymers (see Figure 1). For a better comparability of the data, the block lengths of all the polystyrene block are almost identical. The first polymer (PSB-I) has a shorter polybutadiene block ($m \approx 435$, $n \approx 109$), while the second polymer (PSB-II) has a longer polybutadiene block ($m \approx 423$, $n \approx 390$). Both blocks have polydispersity indices of $U < 1.03$.

PSB-I represents the "classical" surfactant geometry where the binding tail is smaller than the solvating part. This situation is different for PSB-II where both blocks have about the same length.

All chemicals used were purchased from Aldrich Co.

II.2. Epoxidation of the Polybutadiene Block. The block copolymers were epoxidized with 3-chloroperbenzoic acid (MCPBA) in toluene.[16] MCPBA (1 g; ≈60%) was dissolved in 33.15 mL of toluene and dried over Na_2SO_4. Depending on the block length of the polybutadiene block, a calculated amount of the clear solution (8.8 mL in case of PSB-I and 12.5 mL in case of PSB-II) was given to 0.25 g of the block copolymer. The resulting mixture was stirred overnight at room temperature. The polymers were precipitated in methanol, reprecipitated in petroleum ether, and dried in vacuum at room temperature (EPSB-I and EPSB-II).

II.3. Modification of the Polyepoxide Block Catalyzed by $LiClO_4$. The epoxidized block copolymers were modified by a refined method from Macchia et al.[17] The used nucleophile (10.30 mmol in the case of EPSB-I and 27.20 mmol in the case of EPSB-II) and anhydrous $LiClO_4$ (1.028 mmol in the case of EPSB-I and 2.72 mmol in the case of EPSB-II) were dissolved in 5−10 mL of THF (abs). The solution was heated to boiling temperature with the aid of an oil bath. Into the stirred, hot reaction mixture was added dropwise a solution of 0.5 g of epoxidized block copolymer (0.5 g of EPSB-I ≈ 1.03 mmol of epoxy groups; 0.5 g of EPSB-II ≈ 2.72 mmol of epoxy groups) in 5−10 mL THF (abs). The resulting yellow to brown solution was stirred in its sealed flask at 65 °C overnight (16−24 h). The polymer was precipitated in petroleum ether, washed with methanol twice, and reprecipitated in petroleum ether. The resulting white polymer was dried in vacuum at room temperature.

II.4. Modification of the Polyepoxide Block by Benzoic Acid. This modification reaction has been described by Brosse et al.[16,18] Modification with benzoic acid was done with EPSB-I only. Benzoic acid (8.19 mmol) and 1.42 mmol of pyridine were dissolved in 5 mL of THF (abs) and heated to 70 °C with the aid of an oil bath. To this stirred, hot reaction mixture was added dropwise a solution of 0.5 g of EPSB-I (≈1.03 mmol of epoxy groups) in 5 mL of THF. The resulting solution was stirred in its sealed flask at 65 °C overnight. The polymer was afterward precipitated in petroleum ether, washed with methanol twice, and reprecipitated in petroleum ether. The white polymer was dried in vacuum at room temperature.

II.5. Modification of the Polyepoxide Block by Acid Chlorides. For this modification reaction on polyepoxides, we followed the description by Nishikubo and Kameyama.[19] The used acid chloride (4 mmol in the case of EPSB-I and 8 mmol in the case of EPSB-II) and anhydrous tetraethylammonium chloride (dried over P_4O_{10}; 0.4 mmol for EPSB-I and 0.8 mmol for EPSB-II) were suspended in 5−10 mL of THF (abs.) and heated to boiling temperature with the aid of an oil bath. To this hot, stirred suspension was added dropwise a solution of 0.5 g of epoxidized block copolymer (0.5 g of EPSB-I ≈ 1.03 mmol of epoxy groups; 0.5 g of EPSB-II ≈ 2.72 mmol of epoxy groups) in 5−10 mL of THF (abs). The resulting solution was stirred at 70 °C overnight. The polymer was precipitated in petroleum ether, washed with methanol twice, and reprecipitated in petroleum ether. The white product was dried in vacuum at room temperature.

II.6. Solubilization of Metal Salts and Preparation of Metal Colloids. In each case a micellar solution of the used polymer in toluene was prepared ($c = 1$ g/L). Metalation of the micelles was performed by simple mixing of the block copolymer solutions with the desired metal salts. Although most metal salts do not dissolve in toluene, solubilization assisted by the amphiphilic copolymers (dissolution in the micelle core) was readily obtained. This is somewhat unexpected, but might be made clear by the analogous washing process where oil is spontaneously dispersed in water in a micellar fashion. In common cases all the metal salt was solubilized during simple stirring overnight. In general, we used a ratio of metal ion to ligand group from 1:4 up to 1:2.

It must be underlined that this reaction route is not restricted to the above, given rather low polymer concentration which was chosen for purely economical reasons. In experiments which were performed to explore a possible commercial application, polymer concentrations of up to 100 g/L were tested, essentially without changing the collidal properties and the stability of the system.[20]

For the preparation of metal colloids in block copolymers, we followed the procedure given in our previous publication.[9] All metal salt containing micellar solutions were handled in an inert gas atmosphere (Ar). The solutions of metal salt containing micelles were vigorously stirred during the addition of the reducing agents hydrazine ($N_2H_4 \cdot H_2O$) or superhydride ($LiBEt_3H$, 1 M in THF). Only a few drops of the reducing agent already lead to metal colloid formation which was accompanied by a color change. After colloid formation, no further purification according to the side products of the reduction was performed. Since they are rather polar acids (HCl, $HClO_4$, CH_3COOH), it is expected that they stay close to the micelle core, especially when base functionalities were incorporated.

II.7. Dynamic Light Scattering. Dynamic light scattering experiments were carried out in toluene at 20 °C using a Nicomp C370 particle sizer, which directly gave the micelle size and distribution. The solutions were filtered through 0.45

Table 1. Nucleophilic Opening Agents, the Resulting Polymer Samples, and Their Micellar Characteristics in Toluene[a]

modification with	name of polymer	solubility in THF	micelle size in toluene
diethylamine	A-PSB-I	good	no micelles observed
morpholine	M-PSB-I	good	$d = 116.8$ nm, $\sigma = 0.338$
N-methylpiperazine	NMP-PSB-I	good	$d = 120.2$ nm, $\sigma = 0.329$
ethanol (methylamine)	EA-PSB-I	good	$d = 155.5$ nm, $\sigma = 0.366$
ethylendiamine	EDA-PSB-I	gelation, insoluble	
2-mercaptobenzothiazole	MBT-PSB-I	good	$d = 52.7$ nm, $\sigma = 0.312$
	MBT-PSB-II	slow	$d = 208.2$ nm, $\sigma = 0.235$
2-mercaptopyridine	MP-PSB-I	good	$d = 123.4$ nm, $\sigma = 0.327$
	MP-PSB-II	slow	$d = 153.0$ nm, $\sigma = 0.189$
benzoic acid	B-PSB-I	good	$d = 116.0$ nm, $\sigma = 0.346$
benzoyl chloride	BC-PSB-I	good	no micelles observed
4-nitrobenzoyl chloride	NO-PSB-I	good	$d = 101.3$ nm, $\sigma = 0.370$
	NO-PSB-II	slow	$d = 134.5$ nm, $\sigma = 0.240$
4-cyanobenzoyl chloride	NC-PSB-I	good	$d = 83.5$ nm, $\sigma = 0.209$
	NC-PSB-II	good	$d = 134.6$ nm, $\sigma = 0.344$
2-thiophenecarboxylic acid chloride	Thio-PSB-I	good	no micelles observed
	Thio-PSB-II	good	$d = 76.5$ nm, $\sigma = 0.330$
P-chlorodiphenylphosphine	Phos-PSB-I	good	no micelles observed
	Phos-PSB-II	good	$d = 85.6$ nm, $\sigma = 0.460$

[a] d is the diameter of the micelles, as determined with dynamic light scattering. σ is the relative width of a Gaussian distribution fitted to the relaxation curve and illustrates the polydispersity of the samples.

μm Millipore filters; the final concentrations for measurements were between 0.01 and 1 g/L.

II.8. Spectroscopic Techniques and Electron Microscopy. UV measurements were performed with an UV-IKON 931 instrument (Kontron), working in a spectral range between 190 and 900 nm. IR spectra were recorded from polymer films with a Nicolet Impact 400 FT-IR spectrometer working in range between 4000 and 400 cm^{-1}. ^{1}H-NMR spectra are recorded with a Varian 400 MHz spectrometer.

Samples for electron microscopy were prepared by suspension preparation. Dilute micellar solutions were sprayed on a 400-mesh carbon coated copper grid; the nonmetalated micelles were shadowed with Pt/Ir after evaporation of the solvent. Electron microscopy was done on a Tesla BS 500 electron microscope operating at 90 kV.

II.9. Polymer Characterization. GPC measurements are performed in THF (60 °C) with a column combination $10^6-10^5-10^3$ Å from PSS Co. The signals are detected with a two-detector combination (UV: TSP UV1000; RI: Optilab 903).

GPC measurements are performed in DMF (70 °C) with a column combination $10^6-10^4-10^3$ Å from PSS Co. The signals are detected with a two-detector combination (UV: Spectra Physics 100; RI: Gynkotek SE-61).

In addition, the composition of the block copolymers is determined by ^{1}H-NMR and IR spectroscopy.

III. Results and Discussion

In a first step, we optimized the epoxidation reaction of polystyrene-*b*-polybutadiene copolymers. Attemps to epoxidize the blocks with methyltrioctylammonium tetrakis(diperoxotungsten)phosphate(3−) and H_2O_2 failed.[21] GPC measurements of the oxidized samples showed an unacceptable high degree of cross-linking, and in most cases, even insoluble polymers were obtained. Better results were obtained with the epoxidation by MCPBA in toluene. The molecular parameters of the epoxidized block copolymer were determined by DMF-GPC, IR spectroscopy, and ^{1}H-NMR. The NMR spectra of the final products do not show any olefinic proton signals, which indicates an almost quantitative epoxidation. GPC measurements, which are shown below, prove that only a small amount of high molecular weight (cross-linked) polymer is formed. K. Udipi[22] supposes an acid catalyzed cross-linking reaction during the epoxidation process forming high molecular weight polymer. Solvent and concentration have a strong effect on the degree of cross-linking. We tested several other solvents (e.g., $CHCl_3$, CH_2Cl_2), but toluene turned out to be best.

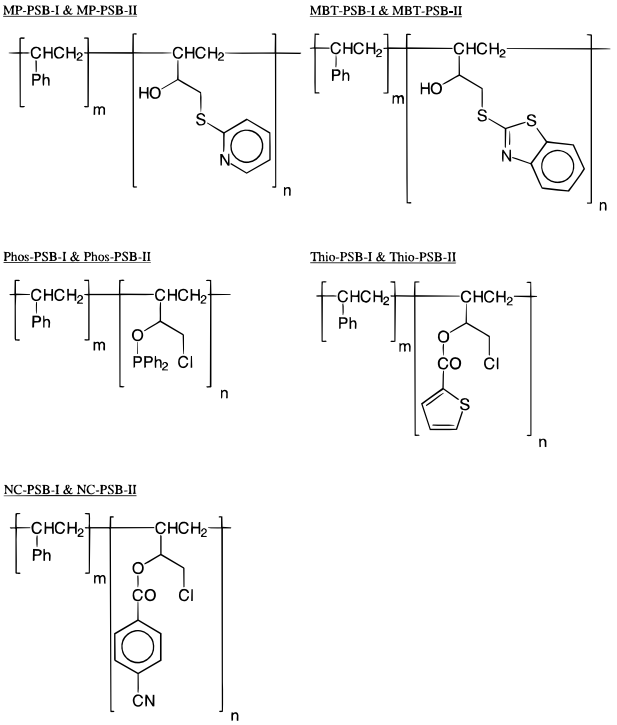


Figure 2. Structural formulas of some of the the ABC's synthesized via addition of commercial nucleophiles.

None of the epoxidized block copolymers showed micelle formation in THF or toluene. This was expected, since both blocks exhibit in this case very similar cohesion energies, i.e., they are of similar hydrophobicity.

In a second step, we modified these polyepoxide blocks by ring opening reactions with several nucleophiles, benzoic acid or acid chlorides. In Table 1 all modification reactions are summarized. For better illustration, some of the related structural formulas of the products are sketched in Figure 2.

The resulting products were characterized by ^{1}H-NMR, by IR, and—if possible—by DMF-GPC. The relative intensities of the NMR signals are in good agreement with the expected values. Completeness of modification is also confirmed by the absence of epoxy group proton signals. DMF-GPC measurements were

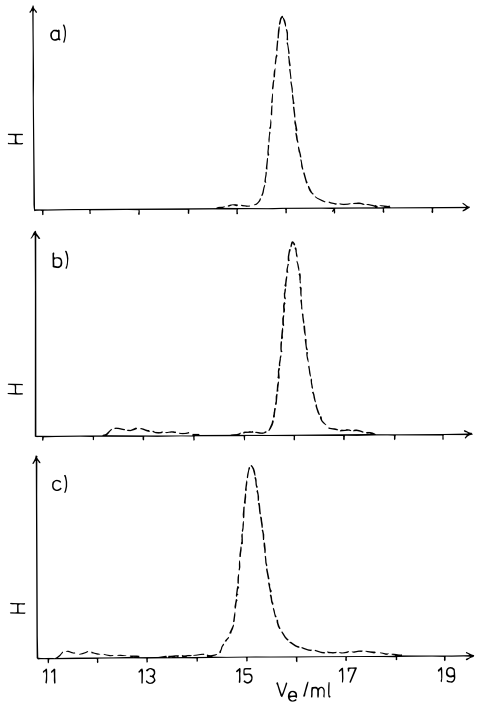


Figure 3. GPC elugrams of samples PSB-I (a), EPSB-I (b), and BC-PSB-I (c). During epoxidation, a small cross-linked fraction (in panel b, eluted close to the excluded volume, V_e = 11 mL) is formed. The ring opening with benzoyl chloride does not change the molecular weight distribution, but significantly shifts the peak toward smaller elution volumes. This is due to an increase of the hydrodynamic volume caused by the introduction of the large side chains.

only possible in the case of polymers modified by acid chlorides. Here, the amount of high molecular weight polymer did not increase. As shown in Figure 3, we observe a broadening of the main peak (which is probably due to interaction with the column material), but no further increase of the high molecular weight component. The modification of polyepoxides by acid chlorides is obviously free of side reactions which lead to any further cross-linking of the products.

Interestingly, modification with acid chlorides is not restricted to carboxylic acid chlorides; reactions with *P*-chlorodiphenylphosphine are also possible (e.g., Phos-PSB-I).

We also tried to open the oxirane rings with multifunctional nucleophiles, such as ethylenediamine. In all cases, cross-linked products were obtained, thus underlining the importance of suppressing intermolecular reactions during the opening procedure.

In those cases where a proton is transferred and hydroxyl groups are formed during the ring opening, no elution in the GPC experiment in THF as well as in DMF was observed. This is not due to cross-linking, since these products dissolve in a molecular or micellar fashion, as shown by diverse light scattering experiments. It is concluded that this is due to interaction with the column material, which is known to be hardly excluded for amphiphilic materials. In case of BC-PSB-I (opened with benzoyl chloride) and Thio-PSB-I (opened with 2-thiophenecarboxylic acid chloride), this amphiphilicity is in a range that we can handle, and the GPC spectra were very similar to that of the parental product. For comparison, the BC-PSB-I spectrum is also shown in Figure 3c.

The other, more polar block copolymers form well-defined inverse micelles in toluene, the diameter and

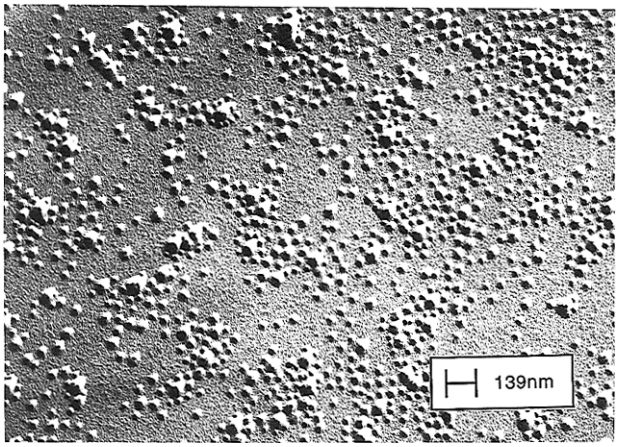


Figure 4. Electron micrograph of the micelles of MPPSB-I, shadowed with Pt/Ir.

polydispersity of which are also given in Table 1. The micelle formation is not restricted to toluene and extends to nearly the whole range of solvents being more polar than cyclohexane. Micelles are even observed in methanol, which are expected to be regular, i.e., the nonpolar chain in the core and the polar parts forming the shell. The micelle size distribution is in the range we regard to be typical for block copolymer micelles.[23]

As expected, block copolymers which are based on the smaller PSB-I also aggregate to smaller micelles. As expected, and as described by simple geometric pictures of micelle formation,[23,24] the micelle size also depends on the chemical nature of the modified polymer block. Typical values for the micelle radius for PSB-I based blocks in toluene lie in the order of 50 −70 nm, where the micelle size increases with core polarity. The micelle radius ought to be compared with the contour length of the outer, solvating polystyrene block, which is on the order of 120 nm. The polymer chains in the micellar environment can therefore be regarded as remarkably stretched where the end-to-end distance is about half of a fully elongated chain.

For MBT-PSB-I and NC-PSB-I, the polarity difference between both blocks is so low and the aggegation so weak that the micelles become comparably small. In case of the weakly or nonaggregating systems, we still can support the formation of micelles by lengthening the polar block. This was demonstrated for the 2-thiophencarboxylic acid chloride and the diphenylphosphine modification where small micelles are just detected for the PSB-II based systems.

The micelle formation can also be visualized by electron microscopy. Figure 4 shows a typical picture characterizing these micelles; due to the lack of contrast, the sample was shadowed with Pt/Ir.

The spherical size of the micelles as well as their rather narrow size distribution is nicely seen. Image processing reveals an average radius of 34 nm. With the known molecular weight of MP-PSB-I, this can be translated into an average aggregation number of $Z \approx$ 1650. This relativiely high aggregation number goes well with the high stretching of the solvating polystyrene chains in the corona and also underlines the very polar character of the micelle core. From the comparison with the diameter as measured by dynamic light scattering (DLS characterizes the micelles in a highly swollen state whereas electron microscopy depicts the solid, collapsed particles), we can estimate an averaged swelling ratio of about 6, i.e., the volume fraction of polymer inside the swollen micelle is 0.17. The quan-

Table 2. Colloidal Characteristics of Different ABC's in Toluene without Metal Salts and Solubilizing a Variety of Noble Metal Salts[a]

sample	d/nm	σ/nm	sample	d/nm	σ/nm
MP-PSB-I			Thio-PSB-II		
without metal salt	123.4	40.3	without metal salt	76.5	25.2
$HAuCl_4 \cdot 3H_2O$	107.8	35.3	$HAuCl_4 \cdot 3H_2O$	148.2	56.3
$AgNO_3$	71.3	38.9	$AgNO_3$	*c*	
$Cu(ClO_4)_2$	134.1	41.9	$Cu(ClO_4)_2$	71.9	16.6
$Pd(OAc)_2$	*b*		$Pd(OAc)_2$	84.3	28.1
$Rh(OAc)_2$	133.6	61.4	$Rh(OAc)_2$	*c*	
$Zn(Cl)_2$	123.4	56.1	$Zn(Cl)_2$	*b*	
MP-PSB-II			Phos-PSB-II		
without metal salt	153.0	28.9	without metal salt	85.6	39.4
$HAuCl_4 \cdot 3H_2O$	209.4	83.7	$HAuCl_4 \cdot 3H_2O$	82.7	41.1
$AgNO_3$	196.0	84.4	$AgNO_3$	*b*	
$Cu(ClO_4)_2$	186.4	45.3	$Cu(ClO_4)_2$	*b*	
$Pd(OAc)_2$	*b*		$Pd(OAc)_2$	90.6	53.4
$Rh(OAc)_2$	133.6	48.0	$Rh(OAc)_2$	*c*	
$Zn(Cl)_2$	300.7	200.7	$Zn(Cl)_2$	*b*	
MBT-PSB-I			NC-PSB-I		
without metal salt	52.7	16.4	without metal salt	83.5	17.4
$HAuCl_4 \cdot 3H_2O$	68.0	32.9	$HAuCl_4 \cdot 3H_2O$	96.34	26.8
$AgNO_3$	86.8	50.7	$AgNO_3$	101.3	35.8
$Cu(ClO_4)_2$	101.7	48.4	$Cu(ClO_4)_2$	*b*	
$Pd(OAc)_2$	56.1	19.3	$Pd(OAc)_2$	*b*	
$Rh(OAc)_2$	63.1	26.1	$Rh(OAc)_2$	*b*	
$Zn(Cl)_2$	57.8	17.6	$Zn(Cl)_2$	132.7	44.7
MBT-PSB-II					
without metal salt	208.2	48.9			
$HAuCl_4 \cdot 3H_2O$	246.9	93.5			
$AgNO_3$	254.2	97.1			
$Cu(ClO_4)_2$	223.4	73.2			
$Pd(OAc)_2$	220.6	125.7			
$Rh(OAc)_2$	252.9	126.7			
$Zn(Cl)_2$	309.4	139.5			

[a] For an explanation of *d* and σ, see Table 1. [b] Combination has not been investigated. [c] Metal salt has not been solubilized.

titative evaluation of other electron micrographs of this series of polymers, the presentation of which is omitted, results in similar values. It is worth mentioning that these data (aggregation number, swelling ratio, and chain stretching) also fit into the behavior of the well-examined case of PS-*b*-P4VP and the simple micelle model presented in the earlier papers.[23,24] Therefore, we conclude that the micelle formation of the more complex amphiphilic polymers presented here also follows the rather simple rules elaborated before, and micelle size can be adjusted by the two block lengths and the interface energy between micelle core and solvent phase, only.

The small fraction of slightly larger micelles seen in Figure 3 might be attributed to the influence the small fraction of high molecular weight, cross-linked polymer, resulting from the epoxidation reaction. On the other hand, we cannot exclude artifacts imported by the sample preparation for electron microscopy.

It was already mentioned that the described ABC's exhibit a substitution pattern based on ligand molecules to enable the binding and uptake of metal salts into organic solvents. Consequently, the micellar solutions of the block copolymers readily solubilize different metal salts which are otherwise insoluble in toluene. Depending on the relative block length of the metal binding block and the substitution pattern of the chelating side unit, the relative amount of metal salt which is solubilized is on the order of at most 5−20 wt %. For technological applications, it is interesting to note that multipodal ligands solubilize larger amounts of salt (for obvious reasons), i.e., we can maximize the relative amount of metal salt by the incorporation of such ligands (e.g., MBT-PSP-I). A number of solubilized salts as well as the characteristics of the resulting metal salt containing micelles are summarized in Table 2.

The micelle size distribution slightly broadens with metal salt uptake. Also the micelle radius seems to increase a little, but no systematic relation between the increase and the polarity of the salt becomes evident. In a different set of experiments, it was shown that the increase of the micelle size even depends on the concrete anion being coupled to the metal,[25] e.g., if Cl^-, ClO_4^-, or CH_3COO^- was chosen. Such side effects are hard to seize and prohibit more quantitative descriptions.

It is also observed that the quality of the ABC's solubilized is different for the different metal ions. The data seem to follow the hard−soft acid−base principle where "soft" cations require "soft" ligands whereas "hard" cations show a distinct affinity to "hard" ligands. This is nicely seen for the technologically relevant case of Pd salts, which require a very soft ligand for solubilization.

Due to the high electron density of the used metal ions, metal salt uptake into the micelle core is easily followed by electron microscopy. Figure 5 shows a typical electron micrograph of such an experiment; the sample is obtained by direct evaporation of a dilute colloidal solution of the metal salt containing micelles (after dissolution of the metal salt crystals) onto the grid. Due to the high electron contrast of the metal salt, further contrasting is not required.

This picture with its "leopard" pattern can be regarded as typical: some structure elements are still in the size range of the original micelles, but also much smaller elements are seen. In addition, we also observe ring-like or banana-like black spots which correspond to the metal salt-containing domains, but not to any micellar equilibrium structure. We attribute this behavior to a wetting−spinodal dewetting transition caused by the carbon film surface during the solvent evaporation which deforms and destroys the original

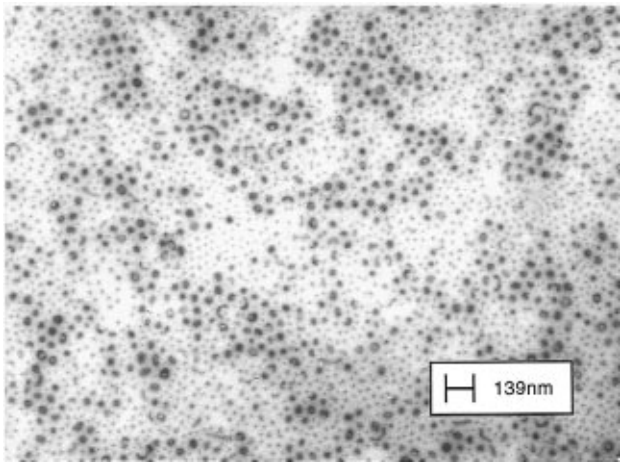


Figure 5. Electron micrograph of MPPSB-I micelles, containing 0.5 mol of $HAuCl_4$ per complexing unit. It is expected that the leopard-skin pattern does not reflect micelle architecture, but is due to a wetting−spinodal dewetting transition caused by the drying process.

micelles. Analogous morphology changes and surface-assisted structure formations were recently described by Möller et al. for similar, gold salt-containing systems.[14]

With these metal salt-containing micelles, we also can demonstrate the usefulness of the "nanoreactor" concept, analogous to earlier work of Cohen,[10,11] Eisenberg,[12,13] or our own previous publications,[8,9] where we have described the synthesis of metal colloids in micelles of polystyrene-*b*-poly(4-vinylpyridine) copolymers. Under certain conditions, it is possible to convert all metal ions of one micelle core (the analogon to a nanometer-sized reaction vessel) to one colloid particle, the size of which is controlled by the micelle size and the relative metal content, only. Our previous system exhibited the disadvantage that only one metal binding site (N) per monomer unit was available, the electronic characteristics of which was fixed. The ABC's described in this paper solve these problems since polymers with several hetero atoms per monomer, an adjustable polarizability, and an improved amphiphilicity (in the general sense) were obtained.

Metal colloids of gold, silver, palladium, and rhodium were prepared from the above-described series of metal salt-containing block copolymer micelles, and it turned out that not all polymers which solubilize the metal salt are able to stabilize the related metal colloid, too. For instance, only Phospho-PSB-II is able to stabilize palladium colloids effectively.

Obviously, we have to use the "soft−hard" principle a second time, and stabilization of a colloidal metal surface is more demanding than uptake of the primary salt. Once the colloid/micelle hybride is formed, their colloidal solutions are nevertheless very stable. With dynamic light scattering, no change of the micelle size and polydispersity is detected, at least over a period of 3 months.

Since this paper is mainly related to the development of the stabilizing block copolymers, we present just shortly the characterization of the colloids by UV−vis spectroscopy and electron microscopy.

Figure 6 shows the plasmon bands of three selected metal colloids (gold, silver, and rhodium; location of the plasmon bands for gold: $\lambda_{max} = 533-550$ nm, silver: $\lambda_{max} = 426$ nm, rhodium: $\lambda_{max} = 367$ nm), as seen in the UV spectra. The width of the peaks and the absence

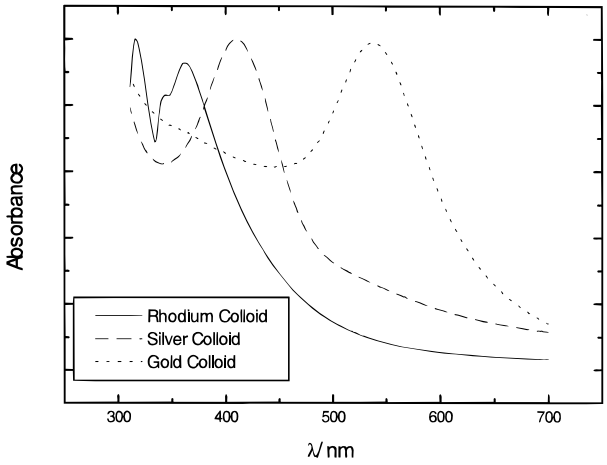


Figure 6. UV−vis spectra of rhodium, silver, and gold colloids stabilized by ABC's.

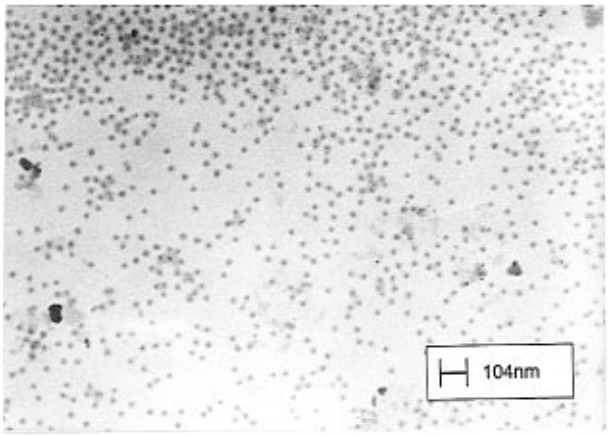


Figure 7. Electron micrograph of rhodium colloids, stabilized with MBTPSB-I. In each micelle, there is just one rhodium colloid, a morphology which we call "cherry"-like.

of other transitions are a measure for the quality and the low polydispersity of our metal colloids being in the 10 nm size range.

The electron microscopy pictures (again without any additional contrasting) show that each micelle contains one metal colloid which is surrounded by the polymer shell, a morphology we have called "cherry"-type morphology.[9] Figure 7 shows the rhodium colloids, stabilized with MBTPSB-I.

Again, the size of the noble metal colloid as well as the overall size agrees with the values obtained by small angle X-ray and light scattering techniques. Up to now, we are unable to differenciate the fine structure of the polymer shell by EM, which should consist of an inner layer of the polar block and an outer layer of the polystyrene chains. We also must recapitulate that electron microscopy on such systems is usually full of artifacts, as discussed above, known from the literature and backed by our own experience. Consequently, all presented results do not rely on single systems, are usually repeated for some times, and are also cross-checked by quantitative small angle X-ray scattering.

It must be underlined that, from all our colloidal solutions, the solvent can be completely removed, thus resulting in solvent cast polymeric films with the properties of the metal colloids. This process is completely reversible: the solid films can be redissolved in all solvents for polystyrene without any significant change of the colloidal characteristics, thus proving the

close-to-perfect stabilization of the metal colloids by the block copolymer shells.

From the viewpoint of catalytical applications, we also performed experiments in cyclohexane which is a Θ solvent for the solvating polystyrene blocks. The switch between a stable colloidal solution at elevated temperatures and a colloidal gel phase at $T < 308$ K is fully reversible and allows a very simple separation of reaction products and the polymer supported colloidal catalyst, which can be reused in the next reaction cycle in the same reaction vessel without any loss and long-winded isolation procedures.

IV. Conclusion and Outlook

We have demonstrated that commercial standard polymers can be modified to amphiphilic block copolymers by simple reactions such as epoxidation. The highly efficient second step of ring opening results in a wide variety of interesting new structures of polymers such as polymers with diphenylphosphine side groups or chelating sulfur and nitrogen ligands. Beside of the delineated examples which were fixed to ligand functionalities, this technique can simply be extended to very hydrophobic (e.g., fluorocarbons) or multifunctional substitution patterns.

Due to their amphiphilicity, these molecules usually dissolve as micelles in diverse organic solvents; their micellar characteristics are very similar to those of other model systems, e.g., polystyrene-*b*-poly(4-vinylpyridine) block copolymers.[9]

The ABC molecules might be used for a wide variety of purposes: the functional side groups can act as tailor-made tack sides for gluing the polymers to surfaces; another application lies in the generation of new polymeric compatibilizers for polymer blends with special interface properties.

In the present paper, we have outlined the usefulness of the micelles of such ABC's as "molecular reactors" for microparticle synthesis with colloidal noble metals as a model system. In a different context, it is shown that the present systems are also able to stabilize nanosized semiconductor particles and ceramic particles.

The resulting colloids stabilized by a thick shell of ABC's can be understood as functional hybrids between polymers and inorganics, where both partners contribute to special material properties. This certainly lies in the combination of chemical functionality of the colloidal cores with the processability of polymers. These hybrids might be useful for simple "low tech applications" like a transparent polymer foil with very high UV absorption (generated by incorporated semiconductor particles), or in more advanced technologies such as photoconductivity or in electro-optical applications.

In spite of these prospects, we feel that research related to ABC's will continue growing to become a key topic of modern polymer chemistry.

Acknowledgment. We thank E. Wenz for numerous discussion and K.T. for steady support with basic chemicals. Financial support by the Max Planck Gesellschaft is gratefully acknowledged.

References and Notes

(1) Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1.
(2) Kennedy, J. P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering*, Hanser Verlag, 1991.
(3) Brittain, W. J. *Rubber Chem. Technol.* **1992**, *65 (3)*, 580.
(4) Tezuka, Y. *Prog. Polym. Sci.* **1992**, *17*, 471.
(5) Meijs, G. F.; Rizzardo, E. *J. Macromol. Sci. Rev.* **1990**, *C30*, 305.
(6) Chung, R. P. T.; Solomon, D. H. *Prog. Org. Coat.* **1992**, *21*, 227.
(7) Riess, G.; Hurtrez, G.; Bahadur, P. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1985.
(8) Antonietti, M.; Heinz, S. *Nachr. Chem., Tech. Lab.* **1992**, *40*, 308.
(9) Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. *Adv. Mater.* **1995**, *7*, 1000.
(10) Ng Cheong Chan, Y.; Schrock, R. R.; Cohen, R. E. *Chem. Mater.* **1992**, *4*, 24.
(11) Yue, J.; Cohen, R. E. *Supramol. Sci.* **1994**, *1*, 117.
(12) Moffitt, M.; Eisenberg, A. *Chem. Mater.* **1995**, *7*, 1178.
(13) Moffitt, M.; McMahon, M.; Pessel, V.; Eisenberg, A. **1995**, *7*, 1185.
(14) Spatz, J. P.; Roescher, A.; Sheiko, S.; Krausch, G.; Möller, M. *Adv. Mater.* **1995**, *7*, 731.
(15) Bates, F. S.; Rosedale, J. H.; Bair, H. E.; Russell, T. P. *Macromolecules* **1989**, *22*, 2557.
(16) Brosse, J. C.; Soutif, J. C.; Pinazzi, C. *Makromol. Chem.* **1979**, *180*, 2109.
(17) Macchia, F.; Crotti, P.; Chini, M. *Tetrahedron Lett.* **1990**, *31*, 4661.
(18) Brosse, J. C.; Klinpituska, P.; Soutif, J. C. *Makromol. Chem.* **1992**, *193*, 315.
(19) Nishikubo, T.; Kameyama, A. *Prog. Polym. Sci.* **1993**, *18*, 963.
(20) Oestreich, S. Diploma Thesis, Marburg, 1995.
(21) Jion, X.; Hay, A. S. *J. Polym. Sci., Chem. Ed.* **1991**, *29*, 1183.
(22) Udipi, K. *J. Appl. Polym. Sci.* **1979**, *23*, 3311.
(23) Antonietti, M.; Heinz, S.; Schmidt, M.; Rosenauer, C. *Macromolecules* **1994**, *23*, 3276.
(24) Förster, S.; Wenz, E.; Zisenis, M.; Antonietti, M. *J. Chem. Phys.*, accepted for publication.
(25) Heinz, S. Doctoral Thesis, Philipps-Universität Marburg, 1993.
(26) Antonietti, M.; Weller, H.; Wenz, E. To be published.

MA951446G