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ORIGINAL CONTRIBUTION

A.W.M. de Laat
H.F.M. Schoo

Novel poly(vinyl ether) block copolymers: Synthesis and colloidal stabilization of α-Fe_2O_3 in water and organic solvents

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A.W.M. de Laat (✉)
Philips Centre for Manufacturing Technology
SAQ 1314
5600 MD Eindhoven
The Netherlands
E-mail: laat_awm@cft.philips.nl

H.F.M. Schoo
Philips Research Laboratories
WB 609
Prof. Holstlaan 4
5656 AA Eindhoven
The Netherlands

Abstract Novel poly(vinylmethylether)-b-poly(vinyloxy-4-butyric acid) diblock copolymers were made for the purpose of colloidal stabilization of particles in liquids. The synthesis via cationic polymerization with HI/I_2 initiation and the characterization of such novel diblock copolymers is described. A set of polymers was prepared including block copolymers with different block length ratios and the two separate homopolymers having the chemical composition of one of the blocks. Colloidal stabilization of α-Fe_2O_3 particles in water could be realized with all polymers except with the poly(vinylmethylether) homopolymer. One of the block copolymers was used for evaluation of the stabilizing abilities in organic solvents. Stable α-Fe_2O_3 dispersions could be prepared in solvents with very different polarities, ranging from methanol to toluene. In addition, it is shown that particles stabilized with these block copolymers can be easily transferred from water to an organic liquid.

Key words Poly(vinyl ether) block copolymers – colloidal stabilization – α-Fe_2O_3 – water – organic solvents

Introduction

In colloid chemistry there is a strong need for powerful stabilizers for the dispersion of particles in liquids. Diblock copolymers can be used effectively, provided that just one of the blocks adsorbs on the surface of the particles and that the other block dissolves in the liquid and does not adsorb [1]. The latter block (the buoy block) then makes up the steric barrier. In steric stabilization the thickness of the adsorbed polymer layer is the key issue [1]. This, in turn, is determined by the block length ratios in the block copolymer [2].

Poly(vinylmethylether) (PVME) is soluble in a wide range of solvents, from the polar lower alcohols to the non-polar aromatic hydrocarbons. It even dissolves in water below 33 °C [3]. Accordingly, a block copolymer with a PVME buoy block is potentially a widely applicable colloidal stabilizer. In addition to the PVME block, an anchor block is needed which provides firm attachment

of the PVME block to the surface of the particles. In principle, the chemical composition of the anchor block will have to be adjusted to the nature of the surface on which it has to adsorb. A chemical composition which is more universally applicable would be profitable. Polyacrylic acid salts are known to adsorb on a variety of surfaces [4–7]. With such an anchor block there is a fair chance that the block copolymer adsorbs on many different surfaces and that a suitable conformation results with protruding PVME chains. Therefore, we decided to use carboxylate groups in the anchor block to stimulate the adsorption.

Living polymerization offers the possibility to synthesize well-defined block copolymers [8]. The vast majority of known block copolymers is synthesized via anionic polymerization [9, 10]. However, with the development of the, e.g. hydrogen iodide/iodine initiator system, living cationic polymerization has shown to be a valuable addition to synthetic polymer chemistry, especially in the synthesis of poly(vinyl ethers) [11–13].

Here we describe the synthesis of well-defined poly(vinyl ether) block copolymers containing a PVME block and a poly(vinyloxy-4-butyric acid) block via a living cationic polymerization [14]. Forder et al. [13] made diblock poly(vinyl ether) copolymers with two uncharged water-soluble blocks. To our knowledge, the block copolymers we present are the first examples of fully water-soluble diblock poly(vinyl ether) copolymers having one ionizable block.

In this paper, the ability of these block copolymers to stabilize α-Fe_2O_3 particles in water and in a variety of organic solvents is presented. The adsorption of the polymers on α-Fe_2O_3 in water and the mechanism of colloidal stabilization was also studied [15]. The temperature-dependent solubility of PVME in water can be employed to gain control over the colloidal stability. We will report on the reversible thermal flocculation of dispersions stabilized with the new block copolymers is due time.

Experiments

Materials

Methylvinylether was obtained from Fluka, and was purified before use by passing the gaseous monomer through a column packed with calcium chloride followed by a column packed with calcium hydride granules. Anhydrous hydrogen iodide was obtained by dehydration of a 57% aqueous solution (Aldrich) with phosphorous pentoxide, and purified by distillation [16], and stored as a solution in *n*-hexane. The solution was sealed in ampules, and stored at $-20\,^{\circ}C$. The concentration of hydrogen iodide was determined by titration [17]. Iodine (Merck) was sublimed twice before use. Dichloromethane, used as a solvent for the polymerization, was distilled from P_2O_5. All other solvents were p.a. grade, and used without further purification.

The PVME homopolymer used for solubility tests, was Lutonal M40 (BASF Ag, Ludwigshafen, Germany), a 50 wt% solution in water. The polymer has number (M_n) and weight averaged molecular weights (M_w) of 20 000 and 60 000, respectively [18].

The α-Fe_2O_3 powder used for the stability experiments was Bayoxide E1352 (Bayer AG, Leverkusen, Germany). The specific surface area was 4.3 m^2/g (BET method) and the isoelectric point (IEP) in water was at pH = 8.0 (potentiometric titration).

Synthesis of ethyl(2-(vinyloxy)ethyl)malonate

All reactions were carried out under dry argon, unless stated otherwise. Ethyl(2-vinyloxy)ethyl)malonate was prepared from 2-chloroethyl vinylether and sodiomalonic ester [19]. In a 1 litre three-necked round-bottomed flask with mechanical stirrer and reflux condenser, 62 g of sodium methoxide (1.14 mol) was dissolved in 500 ml of absolute ethanol. Diethylmalonate (141 ml, 0.93 mol) was added, and the mixture was stirred for 5 min at room temperature. Then 2-chloroethyl vinylether (100 g, 0.94 mol) was added, and the mixture was refluxed for 24 h. After cooling down to room temperature, the heterogeneous mixture was filtered. The solid residue was washed with ethanol. The ethanol was removed from the combined organic layers by evaporation. After dilution with diethylether the raw product was washed with water, concentrated sodium bicarbonate solution in water, and again with water. After drying the solution with anhydrous calcium chloride, the ether was evaporated, and the product vacuum-distilled twice (yield 70.5 g, 0.31 mol, b.p. 110 °C at 7 Torr). The monomer composition and purity were confirmed by ^{1}H-NMR ($CDCl_3$, 300 MHz). The spectrum was in agreement with published data by Sawamoto et al. [20]. Prior to use, the monomer was vacuum-distilled again from calcium hydride.

Polymerization procedure

All reactions were carried out under dry argon, unless stated otherwise. For the polymerization reactions, (standard) Schlenk-type glassware was used. In a typical polymerization experiment, a Schlenk vessel containing 100 ml of CH_2Cl_2, was cooled to $-78\,^{\circ}C$, and 50 ml (40 g, 0.69 mol) of methyl vinyl ether (MVE) was condensed into

it. Hydrogen iodide solution and an equimolar amount of iodine (each 0.84 mmol) were added, and the flask was transferred to a cooling bath kept at −20 °C. The mixture was allowed to react for 24 h, after which a sample was taken. Gas chromatography measurements showed that all MVE was consumed, and size-exclusion chromatography (SEC) showed a nearly monodisperse molecular weight distribution. Next, freshly distilled ethyl(2-(vinyloxy)ethyl)malonate) (8.0 g, 34.8 mmol) was added, and the mixture was stirred for 24 h.

After quenching with ammoniacal methanol, the solution was allowed to warm up to room temperature. The solution was washed with a 10% solution of sodium thiosulfate and with water, and the solvent distilled off. Then, another sample was taken for NMR analysis.

Hydrolysis and decarboxylation of the block copolymers

The resulting polymer was redissolved in a mixture of ethanol and water (5:1) containing 5 g of NaOH, and stirred at 50 °C for 3 h, and concentrated by evaporation. The solution was dialyzed against demi-water for 24 h, followed by 1 N HCl to obtain the free diacid. Next it was diluted with some acetone and heated again at 70 °C for 1 h to complete the decarboxylation. Dialysis against 1 N NaOH converted the material to its salt form. Finally, the product was evaporated to dryness under reduced pressure. ^{1}H-NMR analysis of the polymer showed complete conversion of the malonate moieties.

Dispersing of the α-Fe_2O_3 particles

The α-Fe_2O_3 particles were mixed with the liquid having the required polymer concentration in a polyethylene bottle. Dispersing was done by shaking for 4 h on a Vibrating Energy Mill (VEM) with the aid of 3 mm glass balls added to the dispersion. The volume fraction (ϕ) of the α-Fe_2O_3 in the dispersion was different in the experiments. Data are given in each section.

Characterization

^{1}H-NMR spectra were recorded in $CDCl_3$, D_2O or DMSO-d6 at room temperature on a Bruker 300 MHz. The signal assignment of the block copolymers is based on the ^{1}H-NMR spectrum of ethyl(2-(vinyloxy)ethyl)malonate and on published data for PVME [21]. The signal assignment was confirmed by 2D Homonuclear Shift Correlation Spectroscopy.

For size-exclusion chromatography (SEC) measurements, 20 μl of a 0.5% solution of the polymer was injected on a PLgel-5 μm-MIXED-c column (300 × 7.5 mm, with 50 × 7.5 mm pre column), eluted with THF (LiChrosolv from Merck). An ACS mass detector was used for detection. Calibration was done with standard polystyrene samples.

The rheological properties of the dispersions were measured with the Contraves LS30 equipment (Contraves Ag, Zürich, Switzerland). Flow curves (τ vs. D) from 0 to 115 s^{-1} were measured at a constant temperature of 23 °C. The shear rate was increased in steps and the corresponding force was measured after 15 s equilibration. The straight part of the flow curve was extrapolated to the force axes to determine the Bingham yield value (τ_B), while the slope of this line gave the plastic viscosity η_{Pl}.

An optical microscope (Leitz, Germany) was used to judge the colloidal stability of the dispersions. In a stable dispersion, single particles can be observed in Brownian motion while motionless clumps of particles are present if flocculation occurs.

Results and discussion

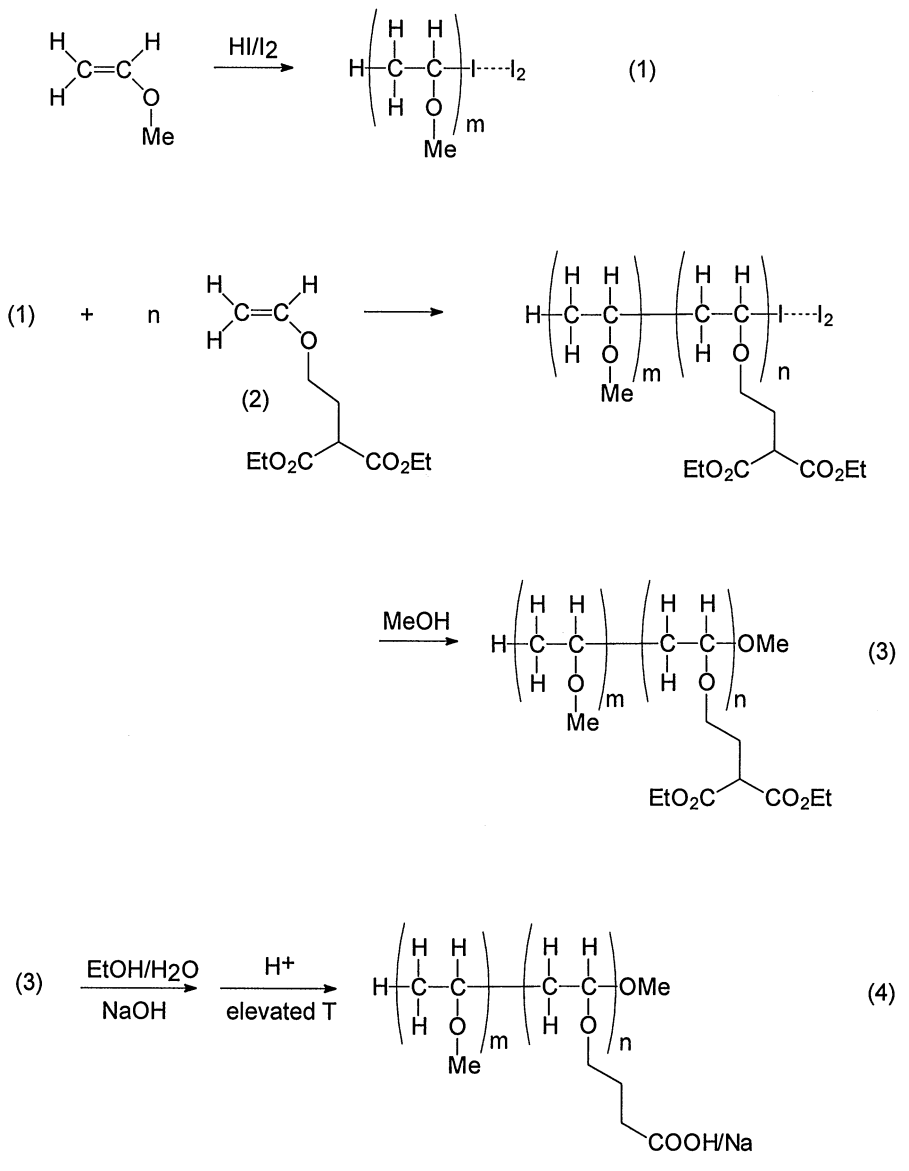
Synthesis of the block copolymers

A proven route to block copolymers with a narrow molecular weight distribution is the cationic polymerization of vinylethers, initiated by I_2/HI [22]. To obtain carboxylate groups in the final polymer, ethyl(2-(vinyloxy) ethyl)malonate was prepared as a monomer. In order to avoid complications due to side reactions during the synthesis of the materials, a protected carboxylic acid functionality was introduced. It is expected that the blocking efficiency is high because of the similarity of the monomers. The route towards the block copolymers is outlined in Scheme 1.

This synthetic route was followed to prepare a series of poly(vinylmethylether)-b-poly(vinyloxy-4-butyric acid) diblock copolymers with different lengths of PVME block, while the poly(vinyloxy-4-butyric acid) (PVOBA) block length was kept more or less constant. In addition, homopolymers representing both separate blocks were prepared. The polymers will be referred to as PE_mA_n. The final set obtained is given in Table 1 below.

These block copolymers do not contain ester linkages as is often present in commercially available stabilizers. PVME is stable in salt solutions, strong alkali and dilute mineral acids. It is, however, unstable in concentrated mineral acids [3, 23]. Accordingly, application at high or low pH values is possible without a risk on decomposition. No interfering effects from large end groups with deviating

Scheme 1 Synthetic route to prepare the block copolymers



chemical composition can occur as these polymers have CH_3 end groups.

Block copolymer characterization

A typical example for the SEC chromatograms of the starting polymer ($PE_{612}A_0$) and that of the corresponding block copolymer ($PE_{612}A_{38}$) is given in Fig. 1. The chromatogram of the block copolymer is slightly broadened and shifted to higher molecular weights but no new peaks have appeared.

The polydispersity of the block copolymers is calculated from the SEC chromatograms (Table 1). In addition, the molecular weights as measured by SEC relative to

Table 1 Characteristics of the block copolymers and homopolymers obtained

PVME-b-PVOBA	Block lengths[a] (m/n)		M_n [$\times 10^3$ g/mol]	M_w/M_n
	m	n		
PE_0A_{50}	0	50	[b]	[b]
$PE_{101}A_{49}$	101	49	[b]	[b]
$PE_{208}A_{42}$	208	42	12	1.2
$PE_{405}A_{45}$	405	45	20	1.1
$PE_{608}A_{42}$	608	42	25	1.3
$PE_{612}A_{38}$	612	38	26	1.1
$PE_{600}A_0$	600	0	28	1.1

[a] See text.
[b] No data because of retention on the column.

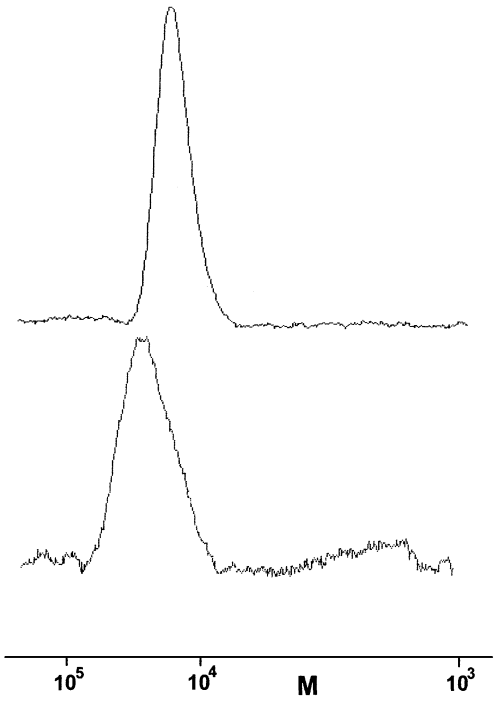


Fig. 1 SEC chromatograms for the starting polymer $PE_{612}A_0$ (top) and the final block copolymer $PE_{612}A_{38}$ (bottom)

polystyrene are given. Note that significant deviations from the actual molecular weights may occur due to differences in the hydrodynamic sizes [13]. Moreover, as the chemical composition of the block copolymers varies, even their mutual differences can only be considered as relative. From the narrow molecular weight distributions found (M_w/M_n) (Table 1), it can be concluded that no termination and chain transfer occurred and the blocking efficiency is high. Obviously, the polymerization indeed follows a living cationic mechanism.

In living polymerization the amount of initiator and the amount of monomer determine the length of each block, assuming all monomers have reacted and no termination or chain transfer occurred. The block lengths are thus fixed by the amounts of monomer used. However, the dosing of the monomers suffered from experimental inaccuracies. Therefore, the block lengths are corrected using the segment ratios in the block copolymer as determined by ^{1}H-NMR, performed on the polymers (3) prior to hydrolysis and decarboxylation. As can be seen in Fig. 2, a number of clearly distinguishable signals are present for the malonic ester residue. The spectra after hydrolysis and decarboxylation are less suitable because some of the signals of the acid monomer unit (PVOBA block) are overlapping with those of the PVME block (Fig. 3).

By integration, the ratio of malonic ester vs. vinyl methyl ether moieties can be determined from the relative intensities of the signals of b/b′ and e, g and h (Fig. 2). To get an indication of the absolute block lengths from this, it was assumed that the overall degree of polymerization was determined only by the ratio of monomer(s)/initiator. The results are given in Table 1.

Complete hydrolysis and decarboxylation is evident from the ^{1}H-NMR spectrum (Fig. 2) as no residual malonic ester functionalities are present.

This analysis shows that the synthetic route employed does result in the block copolymer composition aimed at.

Colloidal stabilization of α-Fe_2O_3 in aqueous solutions

Aqueous α-Fe_2O_3 dispersions were formulated using the block copolymers. The polymer dosage was chosen at a level which was high enough to obtain stable dispersions. The longer the PVME chain, the more polymer was needed. The particles were dispered with the VEM at $\phi = 0.25$. The resulting dispersions are given in Table 2.

Dispersions with low viscosities were obtained with all polymers except with $PE_{600}A_0$, the PVME homopolymer. Dispersion F7 was more viscous which indicates that with $PE_{600}A_0$ at pH = 8.0 the α-Fe_2O_3 dispersion could not be completely stabilized, although some degree of deflocculation was achieved. Without polymer, the α-Fe_2O_3/water mixture with $\phi = 0.25$ is a highly viscous paste at pH = 8 (the IEP). In dispersions F1–F6, the particles could be observed in Brownian motion in an optical microscope after dilution. Accordingly, colloidal stabilization was achieved with all polymers except with the PVME homopolymer.

The stability of these dispersions against salt was studied by dilution of the 25 vol% dispersions to $\phi = 0.15$ at a chosen KNO_3 concentration. The stability of the final dispersions was determined by rheological measurements. Newtonian behavior is found for stable dispersions, while a shear-thinning effect develops, as attraction between the particles becomes noticeable. Typical examples of flow curves for stable (F6) and flocculated (F1) dispersions are in Fig. 4, while further results are given in Table 3.

In many experiments where shear-thinning behavior occurred, the curve had not yet reached a constant slope at the maximum shear rate available with the LS30 equipment. Due to this, the plastic viscosity cannot be determined exactly. A linear fit through the upper part of the curve will result in a too high value of the plastic viscosity. In addition, the maximum shear rate could not be reached with dispersions F2 at 0.03 and 0.1 M KNO_3, and with dispersion F3 at 0.01, 0.03 and 0.1 M KNO_3 due to equipment limitations. The extrapolation is now from a lower part of the curve, causing too low values for τ_B and too high values for η_{Pl}. Although the trends are in the correct direction, the values should be considered as indicative.

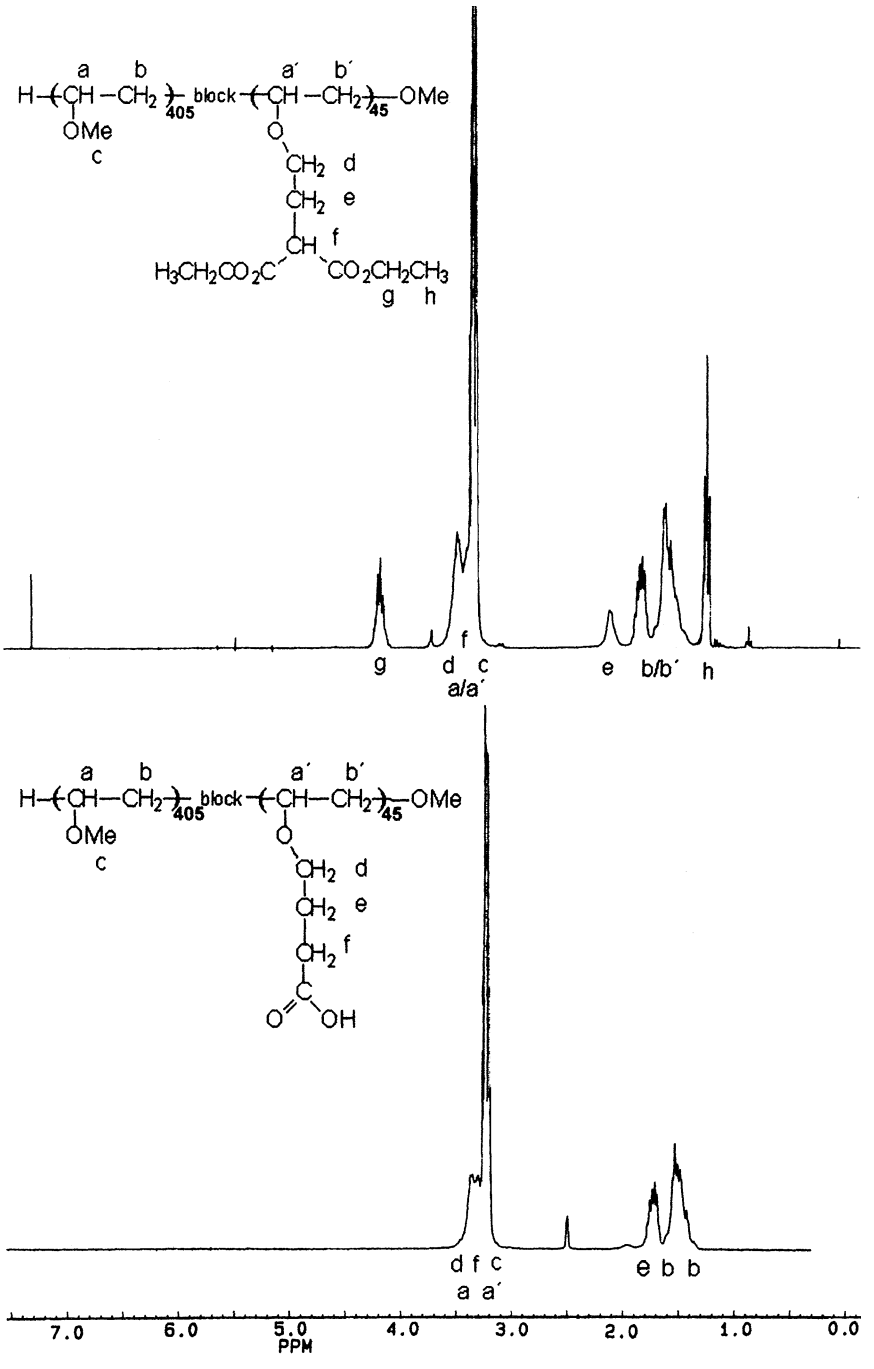


Fig. 2 Typical ^{1}H-NMR spectrum of a PVME-b-PVOBA diblock copolymer. Upper, before hydrolysis; lower, after hydrolysis

Without added salt, the values of τ_B of dispersions F1–F3 are clearly non-zero, although, after dilution, the particles are in Brownian motion. Obviously, there is some interaction between the particles at this higher concentration. The Bingham yield values for dispersions F4–F6 at 0 M KNO_3 are very low, and can be considered to be zero within the experimental error.

Upon increasing the salt concentration, dispersions F1–F3 show some increase in their viscosity and a strong increase in the yield value. With dispersions F4–F6 there is virtually no effect of the salt concentration. The yield values have a negligible magnitude while the viscosities are constant. In these dispersions the block copolymers with the longest PVME chains were used. Obviously, the

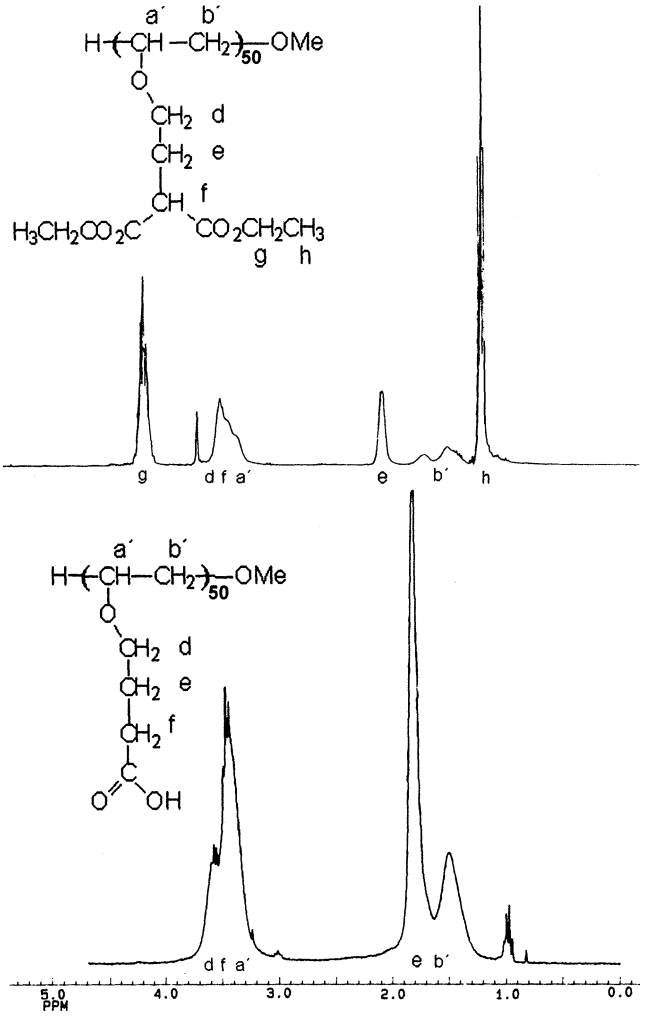


Fig. 3 ^{1}H-NMR spectra of poly(ethyl(2-(vinyloxy)ethyl)malonate) (top) and of PVOBA (bottom)

Table 2 The aqueous α-Fe_2O_3 dispersions

Dispersion	Polymer	Dosage [mg/m^2]	pH
F1	PE_0A_{50}	1	8.7
F2	$PE_{101}A_{49}$	2	7.1
F3	$PE_{208}A_{42}$	2	6.6
F4	$PE_{405}A_{45}$	5	6.0
F5	$PE_{608}A_{42}$	6	7.7
F6	$PE_{612}A_{38}$	5	7.2
F7	$PE_{600}A_0$	5	8.0

dispersions stabilized with PVOBA or a block copolymer with a relatively short PVME chain are sensitive for salt, while the others are not. Flocculation at high salt concentration is typical for electrostatic stabilization, while sterically stabilized dispersions usually are insensitive to the

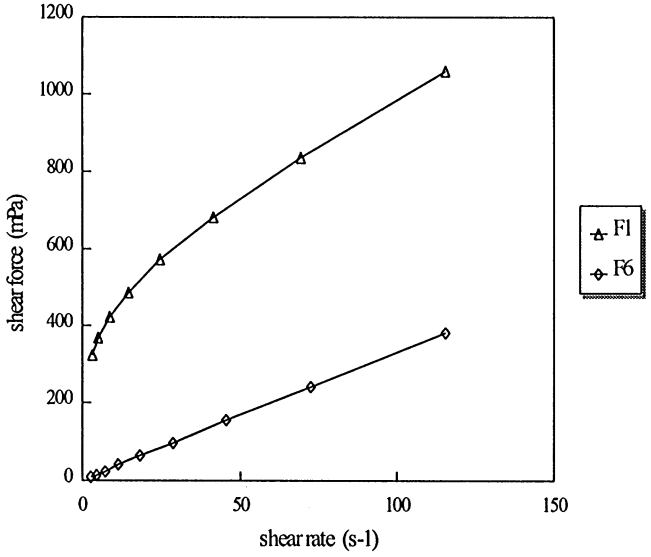


Fig. 4 Flow curves for the α-Fe_2O_3 dispersions. F6 with a Newtonian flow curve; F1 with a shear-thinning flow curve. Both are at $\phi = 0.15$ and 0.1 M KNO_3

salt concentration. These results indicate that different mechanisms of colloidal stabilization are present depending on the block copolymer composition.

Colloidal stabilization in organic liquids

As PVME is also soluble in organic solvents such as alcohols, esters, ketones and aromatic hydrocarbons [3], the block copolymers are potentially suitable as stabilizers in these organic liquids. $PE_{612}A_{38}$ in its acid form was used for these experiments. The ability of this block copolymer to stabilize α-Fe_2O_3 particles in a range of organic solvents with different polarities was compared with the solubility of PVME in these solvents. In addition, reference tests were done without polymer.

The dissolution of PVME in each solvent was tested by trying to make a 1 wt% solution with Lutonal M40 (PVME homopolymer). After evaporating the water from this commercial product in vacuum at 60 °C, the organic liquid was added and the bottle was placed on a roller bench to have sufficient mixing. The dissolution was judged visually after 1 to 2 days of mixing. Results are in Table 4.

To reduce the amount of labor in the stability tests, a dispersion of α-Fe_2O_3 particles in methanol stabilized with the block copolymer was mixed with solvent and then the stability was judged. A concentrated, 72 wt%, dispersion of α-Fe_2O_3 in methanol was prepared on the VEM using $PE_{612}A_{38}$ at a dosage of 4.7 mg polymer/m^2 of

Table 3 Viscosities and yield values from α-Fe_2O_3 dispersions at various KNO_3 concentrations

Dispersion	KNO_3 concentration [M]							
	0		0.01		0.03		0.1	
	η_{Pl} [mPas]	τ_B [mPa]	η_{Pl} [mPas]	τ_B [mPa]	η_{Pl} [mPas]	τ_B [mPa]	η_{Pl} [mPas]	τ_B [mPa]
F1	2.44	64	2.64	98	3.68	143	4.73	508
F2	2.58	69	2.94	112	3.58	143	3.96	174
F3	3.21	51	4.67	100	6.12	141	7.07	172
F4	3.80	4.5	4.46	6.1	4.18	5.7	4.11	5.5
F5	2.68	2.1	2.66	2.2	2.64	2.2	2.66	2.2
F6	3.31	2.3	3.44	3.1	3.41	2.9	3.30	3.0

Table 4 Colloidal stabilization of α-Fe_2O_3 in organic liquids

Solvent	Solubility of PVME	Stability of α-Fe_2O_3 with $PE_{612}A_{38}$			Stability of α-Fe_2O_3 without polymer
		Stab. after mixing	Stab. after evaporation	Flow curve	
2-propanol	+	+	+	N	−
1-butanol	+	+	+	N	−
1,2-propanediol	−	−	−	S-T	−
Methylethyl ketone	+	+	+	N	−
Propylene carbonate	−	+	+	N	−
Butyl acetate	+	+	+	N	−
Butyl lactate	+	+	+	N	−
γ-butyrolactone	+	+	+	N	±
1-methyl-2-pyrrolidone	+	+	+	N	+
Toluene	+	+	+ *	N	−
Cyclohexane	−	−	−		−
Decane	−	−	−		−

+: stable dispersion/soluble.
−: flocculated dispersion/insoluble.
*: some flocs present.
N: Newtonian flow curve.
S-T: Shear-thinning flow curve.

surface as stabilizer. A stable, low viscous dispersion was obtained. This dispersion was diluted with the chosen solvent to 20 wt% of α-Fe_2O_3 . After mixing for 1 day, the stability was judged by microscopic observation of the particles in the dispersion.

After mixing, the sample was kept at 60 °C in vacuum (175 mbar) for 2 h to remove the methanol. For the methylethylketon sample, 0.5 h was taken because of the low boiling point. The weight loss was at least 80% of the amount of methanol present in the dispersion, but most samples had a weight loss higher than the amount of methanol present. Since methanol has the lower boiling point in all dispersions prepared, it can be assumed that nearly all methanol was removed by this procedure. An amount of solvent equal to the weight loss was added to bring the α-Fe_2O_3 concentration back to the initial 20 wt% of the dispersion. After one night of mixing on a roller bench, the stability was again judged by microscopic observation. In addition, flow curves were measured. A Newtonian behavior (viscosity independent of shear rate) indicates a stable dispersion, while a shear-thinning effect points to flocculation.

In the control experiments, it was tried to disperse α-Fe_2O_3 at 20 wt% in each of the solvents without using the block copolymer. The procedure with the VEM was used as described above. All results are given in Table 4.

Provided PVME remains soluble, the change in polarity of the medium from methanol to the specific solvent did not cause flocculation. Note that no redispersing method was applied! The instability in 1,2-propanediol, cyclohexane and decane is related to the insolubility of PVME in these liquids. In cyclohexane and decane the particles were in a macroscopic precipitate. The instability in 1,2-propanediol was evident from microscopic observation and from the flow curve which had a shear-thinning behavior and a high yield value. No stabilization was

achieved without $PE_{612}A_{38}$, except in 1-methyl-2-pyrrolidone and partly in γ-butyrolactone. These results show that α-Fe_2O_3 can be colloidally stabilized with block copolymer $PE_{612}A_{38}$ in those liquids which dissolve PVME. It is very likely that the PVME chains make up the steric barrier while the PVOBA blocks are expected to adsorb on the surface of the particles. Although there will be hardly any dissociation of the carboxylic acid groups in the organic solvents, the polar interactions of these groups with the oxide surface is probably sufficiently strong.

A remarkable situation was found with propylene carbonate. Although PVME does not dissolve, a stable dispersion was found. As the PVME chain is insoluble in propylene carbonate, it will probably adsorb (or precipitate) on the surface of the particles. Due to the high polarity of propylene carbonate, the carboxylic acid groups may dissociate to some extent. As a surface charge is expected to develop, the stability might be due to electrostatic repulsion.

These results clearly show the applicability of this block copolymer as colloidal stabilizer in a wide range of organic liquids with different polarities ranging from the lower alcohols to toluene.

Transfer of particles from water to an organic solvent

It was shown in the previous sections that the present PVME-based block copolymers can stabilize α-Fe_2O_3 particles in both water and organic solvents. In partition experiments between water and organic solvents, most of the PVME is found in the organic solvent [3]. The behavior of α-Fe_2O_3 particles stabilized with a PVME-based block copolymer in a two-phase system was revealed in the experiment below.

An aqueous dispersion of α-Fe_2O_3 stabilized with block copolymer $PE_{405}A_{45}$ was made according to the previously described procedure. Water was added carefully, as to prevent mixing, to an amount of methylethyl keton (MEK) in a tube (Fig. 5, left). By using a pipette, a drop of the α-Fe_2O_3 dispersion was mixed in the water layer (Fig. 5, middle). All particles were in the aqueous phase. Then, the two-phase system is mixed by shaking manually and allowed to separate again into two phases (Fig. 5, right). The difference in phase volumes before and after mixing is due to the partial solubility of MEK in water. All particles transferred to the MEK layer without any evidence of flocculation. Obviously, the particles stabilized with the PVME-based block copolymer behave similarly as dissolved PVME does. Using this block copolymer as colloidal stabilizer, an easy transfer of the α-Fe_2O_3 particles from water to MEK can be realized.

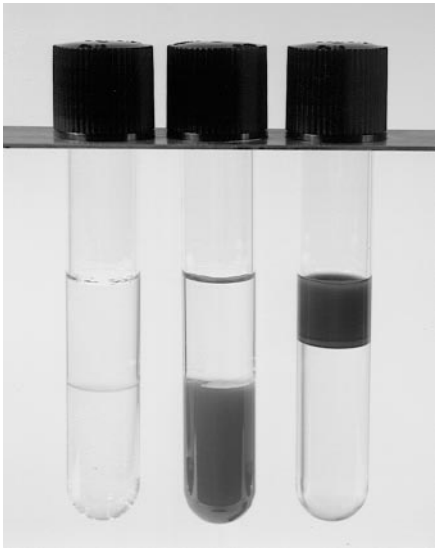


Fig. 5 Transfer of particles from water to MEK. Left tube, the water and MEK layers without particles; middle tube, α-Fe_2O_3 particles mixed in the water layer; right tube, after mixing and phase separation

Conclusions

The synthetic route developed, proved to be very suitable for the synthesis of poly(vinylmethylether)-b-poly(vinyloxy-4-butyric acid) diblock copolymers. A set of block copolymers with increasing PVME chain length and the homopolymers representing both blocks were prepared and characterized. The polymers are suitable for the colloidal stabilization of α-Fe_2O_3 in aqueous solutions. Low-viscous dispersions with 25 vol% of α-Fe_2O_3 were obtained. The stability of α-Fe_2O_3 particles stabilized with block copolymers having a long PVME chain was not influenced by the addition of salt, while with the other polymers an increase in yield value was found. Obviously, steric repulsion dominates with long PVME chains, while electrostatic effects are present with short PVME chains.

Employing the solubility of PVME in a variety of organic solvents, it is shown that the same block copolymers are also powerful colloidal stabilizers in organic solvents. Stable α-Fe_2O_3 dispersions were obtained in alcohols, esters, ketones and toluene. The broad spectrum of solvents for PVME also allows the transfer of α-Fe_2O_3 particles stabilized with the block copolymer from an aqueous phase to an organic solvent.

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