Synthesis of New Amphiphilic Comb-Like Copolymers Based on Maleic Anhydride and α-Olefins

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Summary: Novel amphiphilic comb-like poly(α-olefin-*co*-maleic anhydride) with a controlled ratio of hydrophilic (polyoxyethylene) and hydrophobic (polymethylene) side chains have been synthesized and characterized. The comb-like copolymers are soluble in organic and aqueous media and form micelles whose behaviour could be correlated to the chemical structure of polymers. We foresee that amphiphilic properties of the novel comb-like polymers are obviously the basis of new architectures in solution which could be used in a broad range of applications. Using micelles from these copolymers, silver nanoparticles with a narrow particle size distribution have been obtained as stable dispersion in both polar and non-polar media.

Keywords: amphiphilic comb-like copolymers; poly(α-olefin-*co*-maleic anhydride); silver nanoparticles; solubilization

Introduction

The conformation of comb-like macromolecules in solution may vary from globular to rod-like depending on the temperature or solvent polarity.[1] The structure is determined by: i. backbone composition, ii. side chain composition, iii. grafting density of side chains.[1,2] In solution or adsorbed on a surface comb-like polymers can change their conformation in response to external stimuli such as electric or magnetic field, light, temperature, pH, solvent polarity.[1] The conformational changes provide possibilities for controlling and changing surface composition (upon adsorption). These polymers can be useful for many practical applications such as sensing, drug delivery etc.[1,3]

To respond to changes in environmental polarity, the comb-like macromolecules should contain hydrophilic and lipophilic side chains and also be soluble in both polar and non-polar solvents, which can be achieved through solvation of corresponding fragments.[2] Amphiphilic comb-like macromolecules can undergo microphase separation and form micelles in polar and non-polar solvents.[4]

To synthesize comb-like macromolecules, radical polymerization,[3] as well as polymer analogous reactions of maleic anhydride (MA) copolymers have been used to regulate the density of side chain grafting.[5]

We describe here a new approach to the synthesis of amphiphilic comb-like poly(α-olefin-*co*-maleic anhydride) using polymer analogous reactions, and demonstrate stimuli responsive behaviour of architectures formed by these new copolymers in polar and non-polar solvents. The synthesis described is simple and uses commercially available products.

The proposed synthetic approach consists of two stages. In the first stage, an α-olefin and maleic anhydride undergo radical polymerization to form alternating copolymers. In the second stage, the copolymers are reacted with polyethyleneglycol monomethyl ether (Scheme 1).

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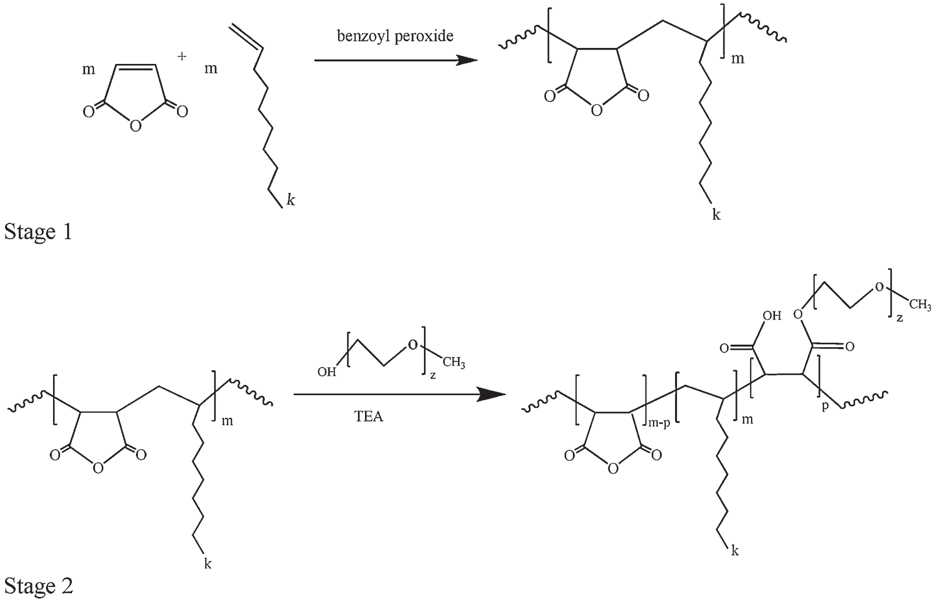

Scheme 1.
Synthesis of amphiphilic comb-like copolymers.

Experimental Part

Materials

1-Octene (O) (Fluka, purum, ≥97.0%) and 1-dodecene (DDC) (Fluka, technical, ≥90%), benzoyl peroxide (Sigma-Aldrich, ~70% (titration)), silver nitrate ($AgNO_3$, Sigma-Aldrich, 99.0%), Nile Red (BioReagent, Sigma-Aldrich, ≥98.0%), Malachite Green (Fluka), maleic anhydride (MA) (Sigma Aldrich, 95%), triethylamine (TEA) (Sigma Aldrich, ≥99%), polyethylene glycolmonomethyl ether (MW = 350, Sigma Aldrich) were used as received. 1,4-dioxane, methyl ethyl ketone and benzene, (99.9%) were purchased from Sigma-Aldrich and used without further purification. Sodium hydroxide and ammonia solution were used as received from Sigma Aldrich.

Polymer Synthesis

The synthesis of poly(α-olefin-*co*-maleic anhydride) was carried out via free radical copolymerization of α-olefin (O, DDC) (1 M) and maleic anhydride (1 M) at 85 °C in 1,4-dioxane solution in sealed vials, under argon using benzoyl peroxide (BP) (0.05 M) as an initiator for 24 hours. The copolymers O-MA and DDC-MA were purified by multiple precipitation in methanol and dried at 60 °C in vacuum to afford a corresponding copolymer in 60% isolated yield.

Amphiphilic copolymers with polyoxyethylene side chains, poly(α-olefin-*co*-maleic anhydride-*co*-methoxypolyoxyethylene maleate), were synthesized by acylation of polyethylene glycolmonomethyl ether (MW = 350, $P_{350}M$) (0.7 M) with poly(α-olefin-co-maleic anhydride) (1.4 M) at 75 °C in 1,4-dioxane (under argon in the presence of TEA as catalyst (0.078 M)). The copolymer was prepared in a round bottom flask with condenser. The reaction mixture (3.1 g of $P_{350}M$, 3.2 g of poly(1-dodecene-*co*-maleic anhydride) (DDC-MA) and 200 µl of TEA dissolved in 30 ml of 1,4-dioxane) was stirred for 6 h in an argon atmosphere. Residual $P_{350}M$ was separated from the solution in methyl ethyl ketone with Millipore water and the remaining polymer was dried in vacuum at 60 °C.

$Ag[(NH_3)_2]OH$ Solution

0.2 g of sodium hydroxide in 1.0 mL of water was added to a solution of 0.12 g of silver nitrate in 1.0 mL of water to give a brown precipitate of silver oxide. The product was isolated by filtration and washed on a filter with Millipore water until the pH of the filtrate was about 8-9. The precipitate was completely dissolved in 0.3 mL of 32% ammonia solution to form a $Ag[(NH_3)_2]OH$ solution.

Silver Nanoparticles

Silver nanoparticles were fabricated in 10, 25 and 50% w/w benzene solution of amphiphilic poly(1-dodecene *-co*-maleic anhydride-*co* – methoxy polyoxyethylene maleate) (DDC-MA-P_{350}M). Equimolar (to P_{350}M side chains) quantities of $[Ag(NH_3)_2]OH$ solution were added at room temperature and the mixture was kept for 24–48 hours without stirring.

^{1}H NMR spectra have been recorded in $CDCl_3$ on a Varian VXR-400 NMR spectrometer.

Molecular weight (MW) of copolymers was determined by gel-permeation chromatography (GPC) using a Waters 515 HPLC pump with an Ultrahydrogel^{TM} 500 7,8 × 300 mm Column (Waters) and a Waters 2410 refractive index detector. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL/min; 200 μL of a 1 mg/mL THF solution were injected for each sample. All samples were filtered through a 0.45 μm THFE filter (Nalgene) during injection. A molecular weight calibration curve was generated with polystyrene standards of low dispersity (Polymer Laboratories, USA).

Optical spectra were recorded on a Cary Varian 100 UV-vis spectrophotometer in the wavelength range from 350 to 800 nm.

Dye Solubilization

Malachite Green and Nile Red solubilization was performed by adding a small amount of dye (solid in case of Malachite Green and 5 μg/mL ethanol solution in case of Nile Red) to 0.5% w/w benzene and aqueous solutions of DDC- MA-P_{350}M respectively. The solubilization was carried out for 24 hours at room temperature.

The hydrodynamic radius of copolymer micelles and the size distribution of silver nanoparticles has been determined by dynamic light scattering (DLS) using Particle Sizing Systems Nicomp 380.

Micrographs of silver nanoparticles were recorded using a transmission electron microscope (TEM) JEOL JEM-100CX.

The composition of the synthesized amphiphilic comb-like copolymers was calculated from the ^{1}H NMR and GPC analyses.

Results and Discussion

On the basis of prior reports on copolymerization of MA and α-olefins, one would expect that these monomers do not homopolymerize in solution.[6–13] However, under specific conditions, at higher concentration of initiator, maleic anhydride forms a homopolymer according to ref.[14–17] Experimental conditions for the synthesis of alternating copolymers from MA and α-olefins have been reported by Y. Tanchuk et al.[18] using α-olefins and MA in 1,4-dioxane at 85 °C in the presence of benzoyl peroxide. Homopolymerization has not been observed under these conditions. Synthesis of O-MA and DDC-MA (Table 1) was carried out as described in ref.[18]

Table 1.
Alternating poly(α-olefin-*co*-MA).

Copolymer	Composition, % mol.		M_n	M_w	PDI
	α-olefin	MA			
O-MA	49.9	50.1	6400	8400	1.31
DDC-MA	49.9	50.1	5800	8000	1.36

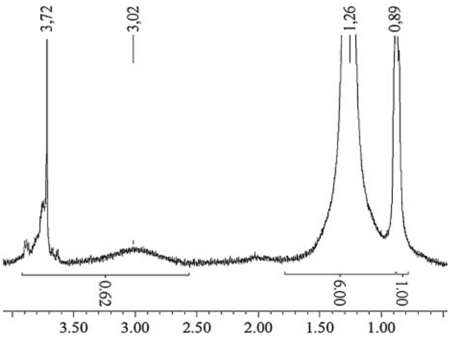

Figure 1.
^{1}H NMR spectrum of DDC-MA recorded in $CDCl_3$.

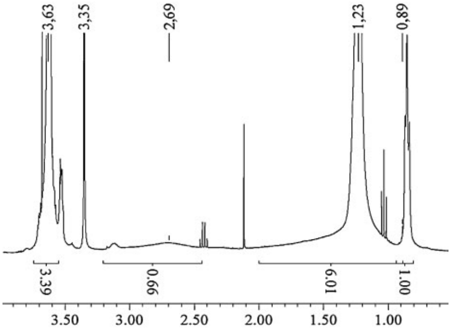

Figure 2.
^{1}H NMR spectrum of DDC-MA-P_{350}M recorded in $CDCl_3$.

^{1}H NMR spectroscopy confirms the structure of O-MA and DDC-MA and the presence of both polymethylene and polyoxyethylene fragments in O-MA-P_{350}M and DDC-MA-P_{350}M.

In the ^{1}H NMR spectrum of DDC-MA copolymer (Figure 1), a peak at 0.89 ppm is attributed to the three protons of the CH_3 group in the DDC unit whereas a peak at 1.26 ppm corresponds to the protons of the methylene groups of DDC. A broad signal in the range from 2.5 ppm to 3.6 ppm is due to the two protons of the CH groups in the maleic anhydride unit. The narrow signal at 3.72 ppm corresponds to the negligible quantities of the residual resident solvent 1,4-dioxane.[19]

Based on integral values of the CH group signal in the MA unit (2.5–3.6 ppm), and the methyl group in the DDC side chain (0.89 ppm), we calculated the MA/DDC units ratio in the DDC-MA macromolecule:

$$(0.63:2)/(1.00:3) = 0.32:0.33 \approx 1:1$$

where 0.63 and 1.00 are signal intensities for the CH in MA and methyl group in DDC units, respectively, and 2 and 3 are the number of protons in the MA unit and DDC methyl group. Thus, the DDC-MA copolymer contains equimolar quantities of the MA and DDC units (50 mol % of each monomer).

As compared to DDC-MA, the following new peaks appeared in the ^{1}H NMR spectrum of the DDC-MA-P_{350}M copolymer (Figure 2): a signal at 3.3–3.4 ppm corresponding to the protons of methoxy end group in the poly(ethylene glycol) side chain and one at 3.4–3.9 ppm attributed to the PEG protons. The latter has been used to estimate the content of PEG side chains in the comb-like DDC-MA-P_{350}M copolymer:

$$(3.40:29)/(1.00:3) = 0.12:0.33 = 0.35:1$$

where 3.40 and 1.00 are integral values of the PEG protons and methyl group in DDC, respectively, and 29 and 3 are the number of protons in the PEG chain (except the methoxy end group) and DDC methyl group. In Figure 2 the signals of the negligible quantities of the residual solvent protons– methyl ethyl ketone appear at 1.03, 2.1, and 2.4 ppm.[19]

Thus, the DDC-MA-P_{350}M copolymer contains 35 mol % of the PEG side chains with respect to the MA units in the DDC-MA copolymer. Hence, the DDC-MA-P_{350}M contains 50 mol % of 1-dodecene, 32 mol % of maleic anhydride, and 18 mol % of methoxy polyethylene oxide units (Table 2).

The amphiphilic comb-like copolymers are soluble both in a polar (water) and a non-polar (benzene) solvent. In dilute solutions the macromolecules are expected to form monomolecular micelles.[20] We determined the value of the hydrodynamic radii, R_h, both in 1% w/w benzene and aqueous solutions of DDC-MA-P_{350}M. The hydrodynamic radius has been found to be

Table 2.
Amphiphilic poly(α-olefin-*co*-MA-$P_{350}M$)

Copolymer	Composition, % mol.			M_n	M_w	PDI
	α-olefin	MA	$P_{350}M$			
O-MA-$P_{350}M$	50	30	20	9900	12600	1.27
DDC- MA-$P_{350}M$	50	32	18	7900	10200	1.28

slightly higher in the polar solvent water (14.0 ± 1.2 nm) than in the nonpolar benzene (10.0 ± 0.8 nm).

To confirm the amphiphilic properties of synthesized copolymers, two dyes, one hydrophobic and insoluble in water (Nile Red) the other hydrophilic and insoluble in benzene (Malachite green) have been selected for solubilization in polymeric micelles. Figure 3 presents the UV-vis spectra of DDC-MA-$P_{350}M$ 0.05% w/v aqueous and benzene solutions showing the successful solubilization of both Nile Red and Malachite Green by polymeric micelles. We expect that solubilization in water and benzene occurs by hydrophobic and hydrophilic copolymer side chains, respectively.

In concentrated solution, polyoxyethylene-containing amphiphilic polymers are known to serve as nanoreactors for the synthesis of silver nanoparticles by reducing silver ions.[21] Figure 4 presents the UV-vis spectra of silver nanoparticles synthesized in concentrated benzene solution of DDC-MA-$P_{350}M$. The concentration of colloidal silver increases with increasing polymer concentration indicating an increase of nanoparticles concentration. Size of nanoparticles remains almost constant regardless of copolymer concentration in benzene (varied in the range 10–50% w/w).

Nanoparticles of very narrow particle size distribution were obtained regardless of the polymer concentration in benzene (Figure 5).

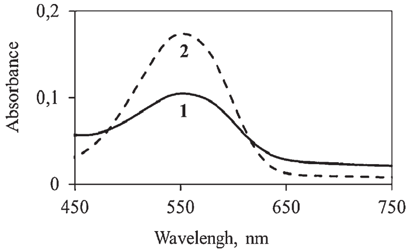

Figure 3.
UV-vis spectra of Nile Red (1) and Malachite green (2) solubilized by 0.05% w/v DDC- MA-$P_{350}M$ solution in water and benzene, respectively.

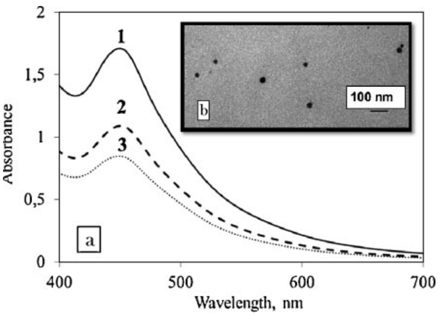

Figure 4.
a - UV-vis spectra of silver nanoparticles synthesized in DDC-MA-P_{350}-M benzene solution: 1 – 50% w/w, 2 – 25% w/w, 3 – 10% w/w; b – TEM image of silver nanoparticles.

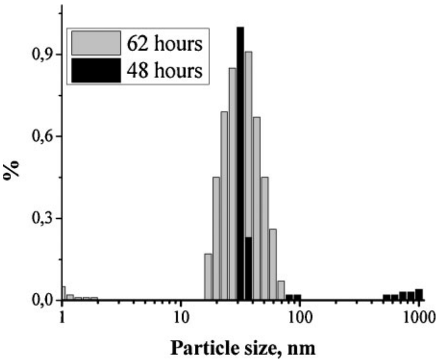

Figure 5.
Size distribution of silver nanoparticles synthesized in DDC-MA-$P_{350}M$ benzene solution, 50% w/w.

Conclusion

We synthesized new amphiphilic comb-like polymers with hydrophobic (polymethylene) and hydrophilic (polyoxyethylene) fragments. The polymers are soluble both in aqueous and organic media, where macromolecules form micelles that reveal inverse behaviour. It is assumed, that polymeric micellar domains serve as stable confined nanoreactors. Silver nanoparticles with a narrow particle size distribution have been synthesized using amphiphilic comb-like polymers in benzene.

Amphiphilic behaviour of the polymers is promising in forming micellar architectures, both in polar and non-polar medium Polymer inverse behaviour can be potentially useful in a broad range of applications.

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