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Polymer 46 (2005) 2020–2028

polymer

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Nanostructures from photo-cross-linked amphiphilic poly(ethylene oxide)-*b*-alkyl diblock copolymers

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Received 18 November 2004; received in revised form 24 January 2005; accepted 25 January 2005

Abstract

Poly(ethylene oxide) monomethylether was functionalized by alkyl chains of various lengths ($l=10$–19 methylene groups) bearing a polymerizable methacrylate moiety. Each synthesis step on the polymer gives quantitative functionalization rates. The self-assembly of the amphiphilic polymers in water was studied by light scattering for various end-groups. Sterical and polar effects were shown to influence the micellization step. The cores of the micelles formed by PEO-C_l-methacrylate were irreversibly cross-linked by UV irradiation. Star polymers that are stable under dilution in good solvent are obtained after 1-min irradiation. The hydrodynamic radius and the molar mass of the nanoparticles depend on the amount of photoinitiator introduced in the cores.

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Keywords: Amphiphilic copolymers; Cross-linked nanoparticles; Poly(ethylene oxide)

1. Introduction

Self-assembly is a promising way to elaborate new macromolecular architectures in a controlled fashion. Amphiphilic block copolymers are known to self-assemble in selective solvents [1,2] and, thus, are good candidates in this purpose. These copolymers, in solution, exhibit a variety of shapes and morphologies that constitute a potential for the formation of novel supramolecular architectures. Spherical micellar structure are often observed for diblock copolymers [1]. However, copolymers with long hydrophobic blocks can display nanotubular [3–5], branched [6,7] or vesicular [8–10] morphologies. The critical micellar concentration (CMC), the aggregation number and the shape depend on the hydrophilic–lipophilic balance [4,11–14], the solvent quality [4,15,16] and the concentration [7]. ABA-type triblock copolymers give flower-like micelles above the CMC and can aggregate to form reversible gels when concentration increases. All these supramolecular architectures are in thermodynamical equilibrium but are reversible. A complete study of their masses, sizes and distribution after dilution requires permanently fixing the structures in the equilibrium state.

Star polymers and nanospheres have been obtained by cross-linking the cores of diblock copolymer micelles. Liu et al. used photochemical reaction to stabilize poly(2-cinnamoylethyl methacrylate) based copolymers in organic medium [17–20]. Poly(ethylene oxide) (PEO) based copolymers bearing polylactide [21], poly(dimethylsiloxane) [22] or poly(1,2-butadiene) [23] as a hydrophobic block were synthesized and cross-linked via thermal, photochemical or γ-irradiation initiations. Ishizu et al. reported the synthesis of polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-PVP) nanospheres that can be used as macro-initiator for the living free-radical polymerization [24,25]. Recently, nanoparticles have been built via intramolecular chain collapse of linear copolymers [26]. Cross-linking of the corona has also been developed for the preparation of PS-PVP knedel-like structures [27,28].

In this work, we report the synthesis of PEO-*b*-alkyl block copolymers bearing polymerizable methacrylate end-groups. This kind of copolymer is well known to give micellar structures for concentrations above the CMC. On this basis, we explore the synthesis of nanoparticles

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doi:10.1016/j.polymer.2005.01.044

obtained by photo-cross-linking of these copolymers in aqueous solution.

2. Experimental part

2.1. Materials

Poly(ethylene glycol) methyl ether (weight average molar mass (M_w) equal to 5 kg mol^{-1}) was purchased from Aldrich and contains 4% w/w of dihydroxytelechelic chains ($M_w = 10$ kg mol^{-1}). 12-Bromo-1-dodecanol (99%), sodium iodide (99%), 3,4-dihydro-2*H*-pyrane (97%), sodium hydride (60% dispersion in mineral oil), methacryloyl chloride (98+%), 2,2-dimethoxy-2-phenylacetophenone (99%) and ethylene glycol dimethacrylate (98+%) were purchased from Aldrich. Amberlyst® 15 and triethylamine were purchased from Acros. Sodium hydride was washed with dry pentane to remove the mineral oil before use. Triethylamine was distilled before use. The other products were used as received. The solvents were dried and distilled before use.

2.2. Characterization

^{1}H NMR spectra were recorded on Brucker AC 400 and Brucker DPX 200 spectrometers using TMS as internal standard.

Light scattering measurements were made using an ALV-5000 multibit, multitau, full digital correlator in combination with a Spectra-Physics laser emitting vertically polarized light at $\lambda = 532$ nm. The temperature was controlled by a thermostat bath to within ±0.1 °C. We have used a toluene standard with Rayleigh ratio 2.79×10^{-5} cm^{-1} at $\lambda = 532$ nm and 22 °C. The specific refractive index increment of the modified and unmodified PEO is 0.135 mL/g [29]. The autocorrelation functions were analyzed in terms of relaxation time (τ) distribution. Measurements were carried out at the angles 30, 60, 90, 110 and 130° and at concentrations of 5 and 10 g L^{-1} (below the critical concentration). Particles were not large enough to present an angular dependence. Experimental errors on molar masses and hydrodynamic radii were estimated by the data dispersion around mean values.

Cryo electron microscopy (cryo-EM) experiments were carried out on a JEOL JEM-2100F, transmission electron microscope. A 300 mesh copper grid coated with a holey carbon film was inserted into tweezers mounted on a plunger [30]. Polymer samples (4 μl) were applied to the grid. After blotting the excess solution (~1–3 s) with filter paper, the plunger immediately immersed the specimen into liquid ethane cooled close to its freezing point using liquid nitrogen [31]. The vitrified specimens were transferred, without reheating, into a Gatan 626DH cryospecimen holder via a cryo-transfer system and introduced into the electron microscope. The particles were observed under low-dose electron beam conditions (~10 e$^-$/Å^2/s) with an acceleration voltage of 200 kV. Micrographs were recorded with a magnification of ×45 000 on Kodak S0163 films. Images were all recorded with a defocus of 2.4 μm, with a defocus variation of ±150 nm. Micrographs were then digitized on a Nikon CoolScan 8000 ED film scanner using a 1200 dpi, corresponding to a scan pitch of 23 μm and to a final pixel size of 4.67×4.67 Å^2 on computer screen.

2.3. Synthesis

The boldface numbers refer to the synthetic route (Fig. 1).

2.3.1. 12-Iodo-1-dodecanol (**1b**)

Synthesized from commercial 12-bromo-1-dodecanol. 12-Bromo-1-dodecanol (18.5 mmol) was refluxed with a large excess of NaI (0.1 mol) in dried acetone (50 mL) for 4 days. Solvent was evaporated and 50 mL of methylene chloride were added. The solution was washed with water, dried over magnesium sulfate and evaporated. The yellow solid was obtained in a quantitative yield and used without further purification. ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (m, 8H, CH_2), 1.55 (qn, 2H, HO–CH_2–CH_2–), 1.82 (qn, 2H, I–CH_2–CH_2–), 3.19 (t, 2H, I–CH_2–), 3.62 (t, 2H, HO–CH_2–).

2.3.2. 2-[(12-Iodododecyl)oxy]tetrahydro-2H-pyran (**2b**)

Compound (**1b**) (11.3 mmol) was dissolved in 3,4-dihydro-2*H*-pyran (22.6 mmol). Amberlyst® 15 acidic resin (1.5 g) was added and the mixture was stirred for 5 h at room temperature. The resin was filtered off and washed with a small amount of methylene chloride. The solvent and the dihydropyran excess were removed under vacuum. The product was purified by flash chromatography (cyclohexane/dichloromethane (respectively (90/10)) and yielded to 10.1 mmol (89%) of (**2b**). ^{1}H NMR ($CDCl_3$) $\delta = 1.20$–2.0 (3m, 26H, CH_2 of dodecyl chain, CH_2 of tetrahydropyranyl (THP) group and I–CH_2–CH_2–), 3.20 (t, 2H, I–CH_2–), 3.30–4.00 (4m, 4H, –CH_2–O–THP+ CH_2–CH_2–O– (THP group)), 4.57 (t, 1H, –O–C*H*CH_2–O– (THP group)).

2.3.3. 2-[(12-Bromododecyl)oxy]tetrahydro-2H-pyran (**3d**)

12-Bromo-1-dodecanol is protected in the same fashion as 12-iodo-1-dodecanol as previously described. ^{1}H NMR ($CDCl_3$) chemical shifts are the same as product **2b**, except the Br–CH_2– triplet at 3.40 ppm.

2.3.4. 6-[12-(Tetrahydro-pyran-2-yloxy)-dodecylthio]-hexan-1-ol (**4d**)

Product **3d** (2.86 mmol) and 6-mercaptohexan-1-ol (3.43 mmol) in 2 mL of distilled *N*,*N*-dimethylformamide (DMF) were degassed and placed under argon atmosphere. A degassed solution of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) was added through a syringe via a septum. The solution was stirred at room temperature for 36 h. The solvent was completely evaporated and dichloromethane

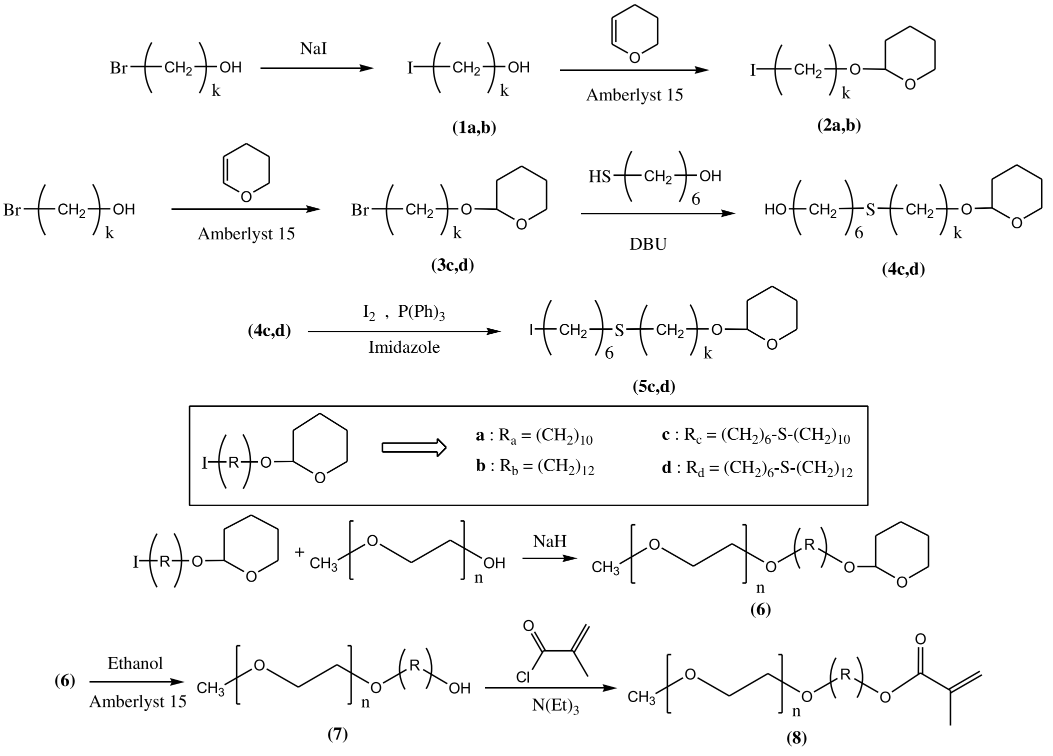


Fig. 1. Synthesis of the diblock poly(ethylene oxide)-*b*-alkylmethacrylate copolymer.

was added. The organic phase was washed with salted water, dried over magnesium sulfate and the solvent was removed under vacuum. The product was purified by flash chromatography (dichloromethane/acetonitrile (respectively (90/10)) and yielded to 2.31 mmol (81%) of (**4d**). ^{1}H NMR ($CDCl_3$) chemical shifts of alkyl chain (between 1.2 and 1.8 ppm) and tetrahydropyranyloxy moiety (between 3.3 and 4.5 ppm) remained the same as for product **3d**. Hydroxyhexylthio group signal appeared: $\delta = 2.50$ (t, 4H, CH_2–S–CH_2), 3.65 (t, 2H, CH_2–OH).

2.3.5. 2- [12-(6-Iodo-hexylthio)-dodecyloxy]-tetrahydropyran (*5d*)

Triphenylphosphine (2.89 mmol) and imidazole (2.89 mmol) were stirred in dichloromethane (8 mL). The solution was cooled to 0 °C and iodine (2.89 mmol) was added portionwise. A pale yellow color and a precipitate appeared. The solution is allowed to warm at room temperature. Product **4d** (2.31 mmol) in 4 mL of dicholoromethane was added dropwise. The solution was stirred at room temperature for 2 h 30 min. The precipitate was filtered off. The organic phase was washed with a sodium thiosulfate solution, dried and evaporated under vacuum. Cold diethyl ether was added and the triphenylphosphine oxide was filtered off. The solvent was evaporated and the same procedure was repeated with cold pentane. A colorless liquid was obtained with 80% yield. ^{1}H NMR ($CDCl_3$) $\delta =$ 3.20 (t, 2H, I–CH_2–), 1.80 (qn, 2H, I–CH_2–CH_2–), the other signals remained the same.

2.3.6. Protected methoxy-PEO-b-C_{12} (*6b*)

The same procedure was used with products **2a**, **2b**, **5c** and **5d**. In a dried round bottom flask under argon atmosphere, sodium hydride (3 mmol) was degassed. A degassed solution of PEO methyl ether (0.6 mmol) in 8 mL of dry acetonitrile was added. The solution was vigorously stirred at room temperature for 2 h. Product (**2b**) (2.4 mmol) dissolved in 2 mL DMF was added dropwise and the mixture stirred at room temperature for 4 days. The polymer was precipitated in diethyl ether, filtered then dissolved in CH_2Cl_2 and precipitated in cyclohexane. The white powder was filtered and dried under vacuum. The polymer was dialyzed versus deionized water for 3 days (membrane cut-off: 3500 g mol^{-1}) and freeze-dried. ^{1}H NMR ($CDCl_3$): chemical shifts of aliphatic protons were identical with (**2b**), I–CH_2– signal disappeared at 3.20 ppm, PEO signals appeared between 3.2 and 4.0 ppm (main peak at 3.64 ppm), 3.36 ppm (s, 3H, CH_3–O–PEO). The integration ratio between the signals of THP group (at 4.57 ppm) and the methoxy group (at 3.36 ppm) allowed an estimation of the functionalization rate.

2.3.7. Methoxy-PEO-b-hydroxydodecyle (*7b*)

Compound (**6b**) (2 g) was dissolved in ethanol (30 mL). Amberlyst® 15 resin (0.5 g) was added. The mixture was stirred 6 h at 50 °C then kept under stirring at room temperature overnight. The resin was filtered off and the solvent removed under vacuum. A small amount of methylene chloride was added to dissolve the polymer and the solution was precipitated in cold diethyl ether. The polymer was filtered, washed with diethyl ether and dried under vacuum. A white powder was obtained in a quantitative yield. The ^{1}H NMR ($CDCl_3$) spectrum showed the disappearance of the tetrahydropyranyl group. The other parts remained identical with those of (**6b**).

2.3.8. *Methoxy-PEO-b-dodecylmethacrylate (**8b**)*

Polymer (**7b**) (0.3 mmol) was dissolved in dry methylene chloride (6 mL). An excess of triethylamine (0.15 mmol) was added. Methacryloyl chloride (0.15 mmol) dissolved in dry CH_2Cl_2 (2 mL) was added dropwise through a cannula. The solution was refluxed for 18 h. After cooling at room temperature, the solution was precipitated in cyclohexane. The white powder was filtered and dried under vacuum. The polymer was dissolved in water and dialyzed versus deionized water for 3 days in the dark (membrane cut-off: 3500 g mol^{-1}). The polymer was then freeze-dried. The final product should be stored in the dark at −18 °C to prevent uncontrolled polymerization of the methacrylate group.

2.4. *Photo-cross-linking*

A solution (5 mL) containing the diblock copolymer at the concentration of 10 g/L, the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) and the cross-linker ethylene glycol dimethacrylate (EGDM) was irradiated with an UVP B-100AP monochromatic ultraviolet lamp (100 W) at a wavelength of 365 nm in a glass tube at a distance of 15 cm. Initiator (5 μL) and cross-linker (5 μL) in separate dichloromethane solutions were added to the aqueous copolymer solution. The whole solution was stirred for 30 min, degassed and placed under argon atmosphere before irradiation.

3. Results and discussion

3.1. *Polymer synthesis*

This work dealing with the synthesis PEO-alkyl diblock copolymers is a preliminary step towards the synthesis of triblock alkyl-PEO-alkyl copolymers. Because of the difficulty to purify this kind of copolymer, it is crucial to optimize the synthesis in order to fully functionalize polymer chains. The strategy of the synthesis was chosen according to the reactivity of the functional groups located on the macromolecules. We first tried to graft 12-iodo-1-dodecylmethacrylate at the end of PEO chains but the competitive transesterification reaction led to poor functionalization rates. In order to avoid this drawback and the uncontrolled polymerization of the methacrylate group, we have introduced the photopolymerizable group in the last step of the synthesis (see Fig. 1). Every reaction on the polymer chains should give quantitative yields to avoid mixtures of functionalized and non-functional chains. The alkyl group, bearing a protected hydroxyl function, was grafted onto PEO chain-ends. The tetrahydropyranyl group used to protect the alcohol moiety is well known to be stable under basic conditions and is easily removed by an acidic treatment [32]. Only, C_{10} and C_{12} bromo-alcohols are commercially available. In order to increase the hydrophobic group length, a *n*-hexyl moiety is grafted to a decyl or a dodecyl chain via a thioether link. The hydrophobicity of thioether link being the same as a methylene group, the lengthened chains can be considered as C_{17} and C_{19} chains owing to the bromo-alcohol used. The hydroxyl group are then converted to iodide moiety according to a procedure previously described [33]. The SN_2 reaction between the hydroxyl function of the PEO and the iodide group was carried out in the presence of sodium hydride. Temperature should be kept low enough to avoid iodide elimination, the rate of the E_2 reaction increasing faster than the SN_2 when temperature increases [34]. The quantitative functionalization of the polymer was confirmed by ^{1}H and ^{13}C NMR. Within the experimental error due to this technique, we observed the complete disappearance of the **C**H_2–OH peak at 61.62 ppm and the protons integration was in good agreement with expected values. After the complete removal of the protective group in the presence of strong acidic resin Amberlyst 15, the methacrylate group was introduced at the chain-end. The classical reaction of the alcohol group on methacryloyl chloride in the presence of triethylamine led to a quantitative functionalization rate after 18 h reflux in dry methylene chloride. Typical ^{1}H NMR spectrum of **8b** is shown in Fig. 2. In addition to the PEO monomethyl ether signals (a: CH_3O–, 3.36 ppm; b: –CH_2–CH_2–O–, 3.60 ppm), the spectrum shows the alkyl chain (c: –CH_2–, 1.20–1.70 ppm; d: –CH_2–OCO–, 4.12 ppm) and the methacrylate group signals (e: CH_3–, 1.92 ppm; f,f′: =CH_2, 5.53 and 6.08 ppm).

3.2. *Micellization step*

Lengthening the hydrophobic chain is well known to increase the aggregation number of the micelles [13,15,35]. However, to our knowledge, the influence of hydrophobic group geometry and/or polarity on the aggregation process of amphiphilic block copolymers in water has not been discussed in the literature. Chain-end effects on the micellization process were investigated at each of the three synthesis steps on the polymer (products **6**, **7** and **8**) for alkyl chain lengths from C_{10} to C_{19}. Static and dynamic light scattering measurements were done at concentrations above the CMC in deionized water (1–10 g/L). Weight-average molar mass (M_w) and *z*-average hydrodynamic radii (R_h) were calculated according to a standard method [36,37]. Aggregation numbers (N_{agg}), defined as M_w of the micelles divided by M_w of the polymer, are summarized in Table 1. It is obvious that chain-ends do not act as simple alkyl groups. The aggregation numbers of PEO-alkyl bearing functional

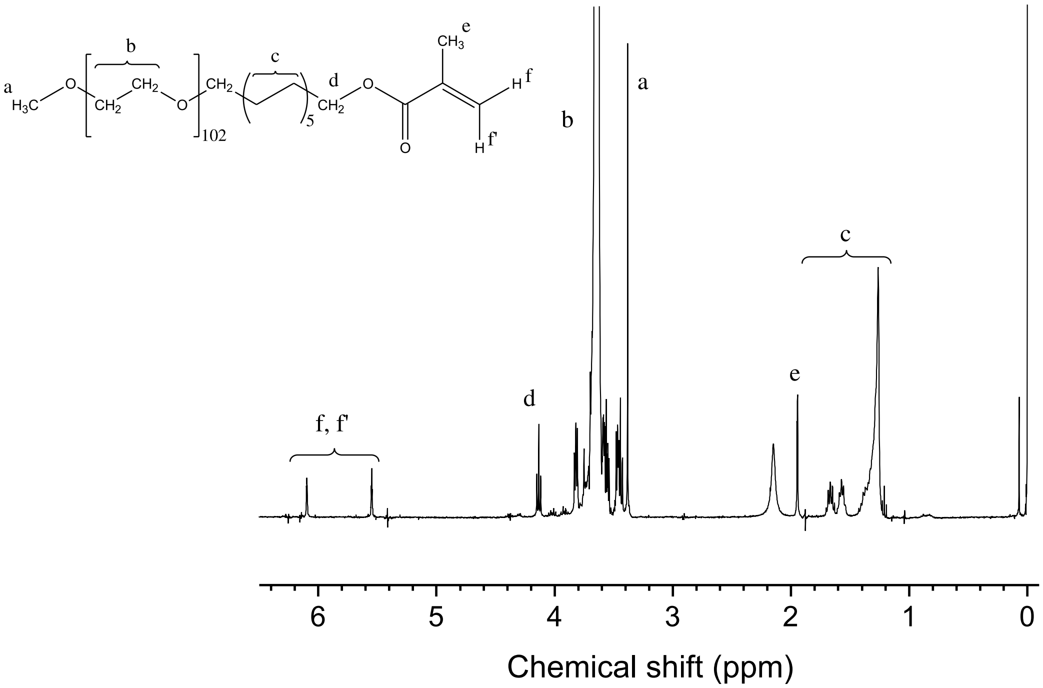
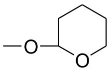
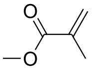


Fig. 2. ^1H NMR spectrum of PEO-C_{12}-methacrylate (**8b**) in $CDCl_3$.

moieties are much lower than those reported by Laflèche et al. [13] on micelles formed by simple PEO-alkyl chains (PEO_{5k}-C_l). Fig. 3 illustrates this observation in the case of PEO-alkyl end-capped with methacrylate group (PEO_{5k}-C_l-methacrylate).

Tetrahydropyranyl groups inhibit micellization for short alkyl groups (C_{10} and C_{12}) and reduces N_{agg} for longer chains (by comparison with an aliphatic chain with the same carbon number). The increased polarity due to oxygen atoms reduces hydrophobic interactions, but the packing effect due to steric hindrance of the six atoms cycle may also play a role. In the case of methacrylate end-group, the combined effects of polarity of the ester function and steric hindrance also reduce the aggregation number compared to simple alkyl groups. However, the effect is less than for tetrahydropyranyl end-groups, probably because the methacrylate end-group is smaller. For hydroxyl end groups, the association is reduced by the hydrophilicity of this moiety.

Table 1
Micellization parameters of hydrophobically modified PEO monomethylether ($M_n = 5000$ g mol^{-1}) in water at 20 °C

Chain-end	Alkyl chain	Aggregation number	R_h (nm)
	C_{10}	1 ± 0.1	2.5 ± 0.1
	C_{12}	1 ± 0.1	2.5 ± 0.1
	C_{17}	15 ± 1	6.6 ± 0.2
	C_{19}	17 ± 1	6.5 ± 0.2
–OH	C_{10}	1 ± 0.1	2.5 ± 0.1
	C_{12}	1 ± 0.1	2.5 ± 0.1
	C_{17}	$3–4 \pm 0.5$	4.5 ± 0.4
	C_{19}	6 ± 0.5	5.0 ± 0.2
	C_{10}	1 ± 0.1	2.5 ± 0.1
	C_{12}	6 ± 0.5	5.5 ± 0.2
	C_{17}	18 ± 1	7.1 ± 0.2
	C_{19}	23 ± 1	7.4 ± 0.2

3.3. UV induced cross-linking

A schematic representation of the cross-linking process is described in Fig. 4. After the formation of micelles in aqueous solution, UV initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) and cross-linker ethylene glycol dimethacrylate (EGDM) were added to the solutions. Melik-Nubarov and Kozlov [38] have already shown that

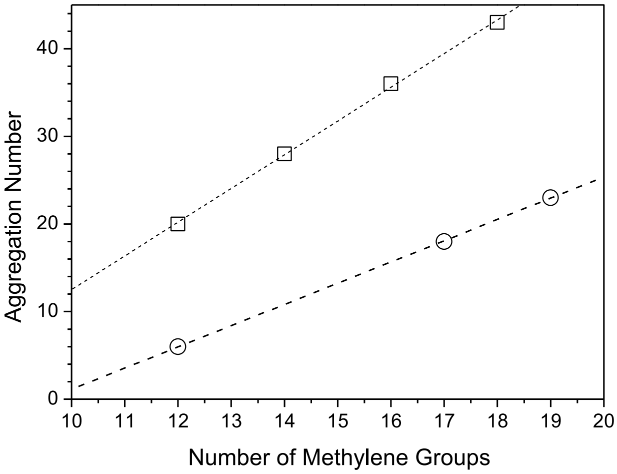


Fig. 3. Aggregation number of PEO_{5k}-C_l-methacrylate (circles) and PEO_{5k}-C_l (squares) as a function of methylene groups number. Dashed lines are linear fits to the data. PEO_{5k}-C_l data were reported by Laflèche et al. [13].

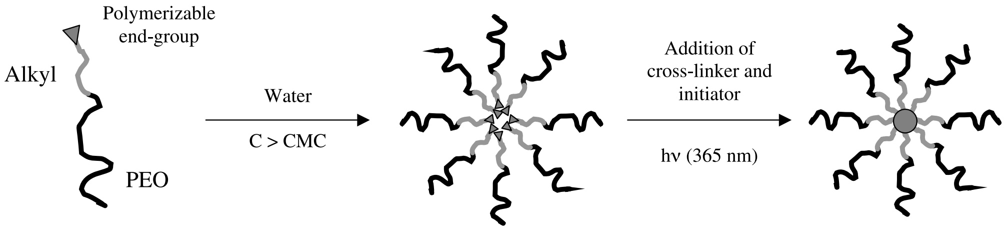


Fig. 4. Schematic representation of the photo-cross-linking process in aqueous solution.

the partition coefficient $P=[S]_m/[S]_w$, i.e. the concentration of solute in the micelles over that in water, of hydrophobic perylene in pluronic micelles was around 200. DMPA and EGDM are hydrophobic and we expect them to be concentrated in the cores. Experiments on POE–C_{12}-methacrylate showed that 70% of the micelles were cross-linked after 10 s. UV exposure, and all the cores are fully cross-linked within 60 s UV. We note that this time is longer than the one reported by Osborn et al. for the photoinitiation of acrylate monomers by DMPA [39,40]. Consequently, all cross-linking was completed by irradiating the samples during 1 min.

Two samples of PEO-C_{12}-methacrylate were prepared at a concentration of 5 g L^{-1} in water with EGDM (20% mol/mol). DMPA (80% mol/mol) was added to one sample, the other being used as a reference. Both trials were irradiated, freeze dried and subsequently dissolved in acetonitrile (a good solvent for both blocks). Static and dynamic light scattering was used to determine the size and the molar mass. In both cases we found a single narrow distribution of relaxation times, see Fig. 5. At the concentration used in the experiment ($C=5$ g L^{-1}), interactions can be neglected and the hydrodynamic radius can be directly calculated from the relaxation time. For the sample without DMPA we found $R_h=2.4$ nm and $M_w=5500$ g mol^{-1} which are equal to that of the non-associated macromonomer in acetonitrile. For the sample with DMPA, we found $R_h=7.3$ nm and $M_w=30\,500$ g mol^{-1}. These results demonstrate that the cores of the micelles can be permanently cross-linked, but only in the presence of a photoinitiator. Fig. 6 shows a typical cryo-TEM picture of cross-linked PEO-C_{12}-methacrylate in water. This micrograph exhibits the spherical structure of the star-polymers obtained after photopolymerization.

Table 2 summarizes the influence of the amount of photoinitiator on the cross-linking. For clarity, the aggregation number after cross-linking has been normalized by the aggregation number of micelles without cross-linker and photoinitiator in water (N^0_{agg}). The mean amount of cross-linker was set to 1 or 2 molecules per micelle. We expect such a small amount not to influence the micellization and photo-cross-linking processes. Fig. 7(a) and (b) show the evolution of N_{agg}/N^0_{agg} as a function of the average number of DMPA molecules per micelle ($DMPA_m$) for PEO-C_{12}-methacrylate and PEO-C_{17}-methacrylate, respectively. Both experiments were carried out with the same molar ratios [DMPA]/[Poly] (0.2, 0.4, 0.6 and 0.8). In the case of C_{12} group before UV irradiation, within the experimental error, no influence of DMPA on the aggregation number is noted until 5 molecules per micelle. For $DMPA_m<3$, an important increase of the aggreation number is observed after cross-linking. The repartition of DMPA molecules in micelles calculated according to a Bernouilli distribution function implies that 29% of the micelles are empty for $DMPA_m=1.2$ and 8.5% are empty for $DMPA_m=2.4$. For $DMPA_m>3.6$, more than 97% of micelles contain DMPA molecules. We think that the radical lifetime is long

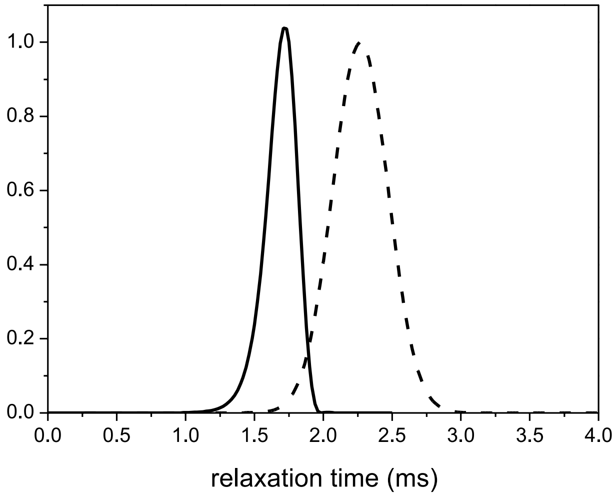


Fig. 5. Normalized relaxation time distribution functions of PEO-C_{12}-methacrylate irradiated by UV light in the presence of DMPA (dashed line) and without DMPA (straight line). DLS measurements were carried out at $C=5$ g L^{-1} in acetonitrile.

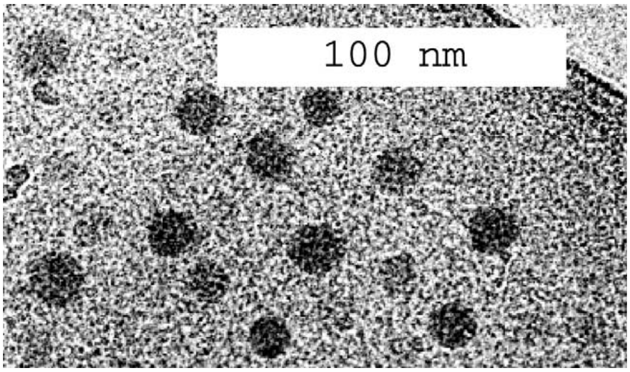


Fig. 6. Cryo-TEM micrograph of cross-linked PEO-C_{12}-methacrylate in water ($C=5$ g L^{-1}).

Table 2
Influence of the initiator amount on the photo-cross-linking process

Alkyl chain	[DMPA]/[*poly*] (mol/mol)	$\mathrm{DMPA_m}$[a]	[*EGDM*]/[*poly*] (mol/mol)	$\mathrm{EGDM_m}$[b]	N_{agg} before UV[c]	R_h before UV (nm)[c]	N_{agg} after UV[c]	R_h after UV (nm)[c]
C_{12}	0.2	1.2	0.2	1.2	6 ± 0.5	5.5 ± 0.1	18 ± 1	–
	0.4	2.8	0.2	1.4	7 ± 0.5	5.5 ± 0.1	11 ± 1	7.5 ± 0.2
	0.6	3.6	0.2	1.2	6 ± 0.5	5.5 ± 0.1	6 ± 0.5	5.7 ± 0.2
	0.8	4.8	0.2	1.4	6 ± 0.5	5.5 ± 0.1	6 ± 0.5	5.7 ± 0.2
C_{17}	0.2	3.6	0.1	1.8	18 ± 1	8.1 ± 0.2	18 ± 1	7.9 ± 0.2
	0.4	7.2	0.1	1.8	18 ± 1	8.1 ± 0.2	23 ± 1	9.1 ± 0.2
	0.6	12	0.1	2.0	20 ± 1	8.3 ± 0.2	30 ± 1.5	9.4 ± 0.2
	0.8	17.6	0.1	2.2	22 ± 1	8.4 ± 0.2	31 ± 1.5	9.5 ± 0.2

[a] Average number of photoinitiator molecule per micelle.
[b] Average number of cross-linker molecule per micelle.
[c] Measured by light scattering in water.

compared to the exchange time of polymers between micelles. Thus, this pseudo-living radical can incorporate new chains that are exchanged from non-initiated micelles. When $\mathrm{DMPA_m}$ reaches the value of 3, the amount of empty micelles becomes negligible and the probability of initiating polymerization in each core increases. Micelles are fixed in their equilibrium state. For C_{17} group, the dimensions of the micelles before cross-linking are not influenced by the addition of cross-linker and initiator until $\mathrm{DMPA_m} \approx 8$. We expect that smaller amounts of initiator do not modify the aggregation number before UV treatment. For higher concentrations of DMPA in the cores, a small increase of the size and the aggregation number is observed. Probably the presence of small molecules in the core reduces the effect of steric hindrance. After UV irradiation, for $\mathrm{DMPA_m} > 4$–5, less well defined and more polydisperse particles are obtained with a higher average aggregation number. This phenomenon may be due to transfer or termination reactions. Indeed, during the propagation step of the photo-cross-linking process, the probability of reaction with DMPA molecules instead of methacrylate groups increases, stopping the core stabilization before all end-groups are cross-linked. Thus, free macromolecules can migrate and can be incorporated into other pseudo-living micelles. For both alkyl chain lengths, in the range $3 < \mathrm{DMPA_m} < 5$, it seems that the size and the aggregation number remain the same before and after cross-linking. Measurements made in acetonitrile confirm that the cores have been polymerized without affecting the micelles size. Even if the available data number is too small to conclude on the universality of this behavior for different chain lengths, we have assumed that DMPA quantities included in this range (3–5 per micelle) should not modify significantly micellization and cross-linking processes.

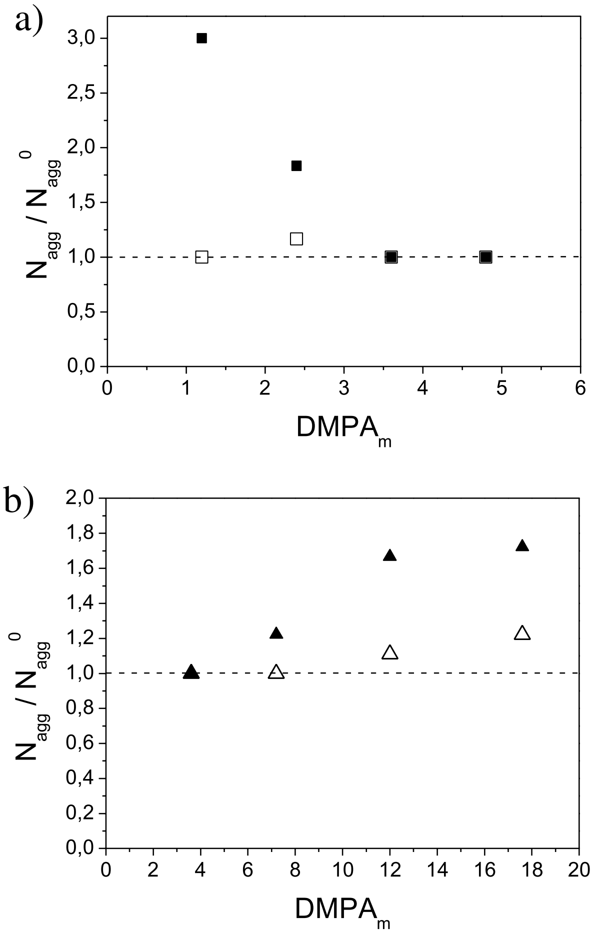


Fig. 7. Reduced aggregation number as a function of the average number of photoinitiator molecules per micelle for: (a) PEO-C_{12}-methacrylate and (b) PEO-C_{17}-methacrylate before (open symbols) and after UV (filled symbols) in water.

The surprising ability of the core to incorporate free chains during the polymerization was also demonstrated by irradiating mixtures of PEO-C_l-methacrylate and PEO-methacrylate. The latter polymer, which does not bear any alkyl group, was synthesized by refluxing monomethylether-PEO and methacryloyl chloride in CH_2Cl_2 in the presence of triethylamine. We checked that PEO-methacrylate does not associate into micelles in water in the concentration range studied here. Table 3 summarizes the influence of UV irradiation on alkylated/non-alkylated polymers mixtures at $C_{mixt} = 10\ g\ L^{-1}$ for C_{12} and C_{19} alkyl chains. Before UV irradiation, it can be assumed that

Table 3
Photo-cross-linking of PEO$_{5k}$-C$_l$-methacrylate and PEO$_{5k}$-methacrylate mixtures

Alkyl chain	% PEO$_{5k}$-meth. (w/w)	DMPA$_m$	Before UV irradiation		After UV irradiation		
			$(N_{agg})_i$	$(R_h)_i$ (nm)	UV time (s)	$(N_{agg})_f$	$(R_h)_f$ (nm)
C$_{12}$	50	3.6	6±0.5	4.7±0.2	30	7±0.5	5.3±0.2
					120	8±0.5	6.4±0.2
C$_{19}$	40	4.6	23±1	7.4±0.2	60	27±1.5	8.4±0.3

PEO-methacrylate does not participate in the micellization process and aggregation numbers are in very good agreement with those found for pure copolymer systems. After UV irradiation, an increase of hydrodynamic radius and scattered light intensity is observed at conditions when they remain constant for the pure copolymer system. The increase of size depends on irradiation time and can be as much as 30%. At the present time, we cannot give satisfactory answers to explain this size increase phenomenon and it remains an open question.

4. Conclusion

Poly(ethylene oxide) has been functionalized by alkyl chains of various lengths bearing photopolymerizable methacrylate moiety. The polymerizable group was introduced during the last synthesis step in order to optimize the polymer functionalization yield. Self-association of the functionalized polymer chains in aqueous solution results in micellar structures. The presence of hindering and/or polar group at the chain-end has been shown to reduce the aggregation number. Stable star-shaped architectures are obtained by addition of initiator and cross-linker and subsequent UV irradiation. The amount of photoinitiator and the presence of non-alkylated PEO-methacrylate were shown to influence the aggregation number after photo-cross-linking.

The synthetic route described here allows the chemical modification of many hydroxytelechelic polymers. Triblock alkyl-*b*-PEO-*b*-alkyl chains bearing methacrylate groups has been synthesized in the same fashion [41]. This polymer gives complex structures in aqueous solution (flower-like, aggregates, networks) owing to the concentration range. These structures being reversible and in thermal equilibrium, their size and distribution analysis are difficult to provide. The ability to cross-link the micelles cores in their equilibrium state could allow the structures study after dilution and, thus, could bring new elements to the understanding of reversible aggregation phenomena.

Acknowledgements

We thank Taco Nicolai for helpful discussions, Nicolas Boisset and Eric Larquet for the cryo-TEM facilities.

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