# METHACRYLATE NANOPARTICLES BY CROSSLINKING OF BLOCK COPOLYMER MICELLES IN ORGANIC SOLVENTS

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## Introduction

Block copolymers are of particular interest, in solution as well as in the solid state, due to their ability to self-assemble. Aggregates formed in selective solvents cover a range of various morphologies, e.g., micelles or vesicles, which depend on many factors like the relative block length, their chemical nature or the type of solvent. The stability of such structures depends on the thermodynamic quality of the solvent and the temperature. Crosslinking is known to be an efficient way to stabilize core-shell micelles. One can crosslink the core[1, 2] or the shell[3] of a micelle. Here, we report about the synthesis and characterization of polybutadiene-*b*-poly(methyl methacrylate) (PB-PMMA) and polybutadiene-*b*-poly(methyl methcrylate)-*b*-poly(2-hydroxyethyl methacrylate) (PB-PMMA-PHEMA) block copolymers, their self-assembly in organic solvents and the characterization of nanoparticles formed by crosslinking of the polybutadiene core.

## Experimental

**Materials**. *Sec*-butyl lithium (*sec*-BuLi) (Aldrich), *iso*-butyl aluminum (2,6-di-*tert*-butyl-4-methylphenolate)$_2$ (*i*BuAl(BHT)$_2$) (Kuraray) were used without further purification. Butadiene (Messer Griesheim) was passed through columns filled with molecular sieves (4Å) and basic aluminum oxide and stored over dibutylmagnesium. Methyl methacrylate (BASF) and 2-(trimethylsiloxy)ethyl methacrylate (Aldrich) were condensed on a vacuum line and stored at liquid nitrogen temperature until use. Toluene (Merck) was distilled from CaH$_2$ and potassium. 1,2-Dimethoxyethane (DME) was purified using a certain amount of *sec*-BuLi and condensed on a vacuum line. S$_2$Cl$_2$ (Aldrich) was used as cross-linking agents without further purification.

**Instrumentation**. Gel permeation chromatography (GPC) measurements were performed on a set of 30 cm SDV-gel columns of 5 µm particles size having a pore sizes of 10$^5$, 10$^4$, 10$^3$ and 10$^2$ Å with RI and UV ($\lambda$=254 nm) detection. THF was used as eluent with a flow rate of 1 ml/min and polybutadiene standards were used for calibration. $^1$H NMR spectra were obtained on a Bruker 250AC spectrometer using CDCl$_3$ as solvent. Dynamic Light Scattering (DLS) measurements were performed on an ALV DLS/SLS-SP 5022F compact goniometer system with an ALV 5000/E correlator and a He-Ne laser. Samples solutions were filtered using Millipore Teflon filters with a pore size of 0.2 µm. CONTIN analysis of the obtained autocorrelation functions was carried out. Transmission electron microscopy (TEM) was performed on a Zeiss electron microscope (CEM 902) operated at 80kV. Samples were stained using OsO$_4$. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) measurements were performed on a Bruker Reflex III instrument.

**Synthesis of PB-PMMA and PB-PMMA-PHEMA.** Sequential anionic polymerization of the PB-PMMA and PB-PMMA-PHEMA block copolymers was carried out in toluene using *sec*-BuLi as initiator. PB was polymerized first at 30 °C. Under these conditions a predominant 1,4-structure is obtained. After the polymerization of butadiene, a mixture of DME and *i*BuAl(BHT)$_2$ was introduced to enable the subsequent polymerization of methyl methacrylate, in a controllable manner at room temperature[4]. For the PB-PMMA-PHEMA triblock, silyl-protected 2-(trimethylsiloxy)ethyl methacrylate (TMS-HEMA) monomer was added directly after the polymerization of the second block at room temperature. Two polymerizations were carried out. Each time an aliquot of the diblock was withdrawn before adding the third monomer. The molecular weight of the PB and PB-PMMA blocks and molecular weight distributions were measured using MALDI-TOF. Molecular weight of the triblocks was determined from the monomer fractions obtained by $^1$H NMR. The deprotection of the TMS-HEMA block was achieved by mixing the reaction solution with aqueous H$_2$SO$_4$.

**Preparation of the micellar solutions.** Acetone, dimethylformamide (DMF) and acetonitrile (ACN) were chosen as selective solvents for PB and micelles with PB core were obtained by directly dissolving the block copolymers in these solvents.
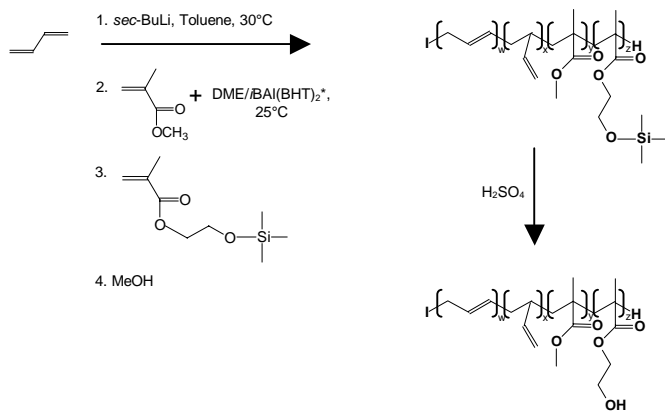


**Figure 1.** Synthesis of PB-PMMA-PHEMA via sequential anionic polymerization (subscripts denote degrees of polymerization for each block).

**Crosslinking of block copolymer micelles**. Crosslinking of PB-PMMA and PB-PMMA-PHEMA block copolymers in selective solvents were carried out, using different crosslinkers at a concentration of 1g/L. S$_2$Cl$_2$ was added to the micellar solution and the mixture was left at room temperature for 24 hours. All the samples were purified by dialysis after reaction. Molar ratios between the butadiene units and the crosslinker were typically 1:0.5, 1:1 or 1:2.

## Results and Discussion

**Synthesis of PB-PMMA and PB-PMMA-PHEMA.** The synthesis of PB-PMMA and PB-PMMA-PHEMA is depicted in **Figure 1**. The GPC traces (**Figure 2**) show narrow molecular weight distribution for the diblock and the triblock copolymers (<1.08). Complete initiation of the second block can also be noticed, no PB precursor was left.
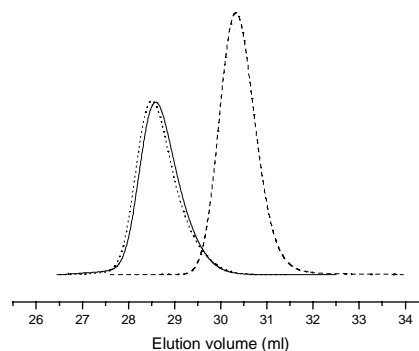


**Figure 2.** GPC traces of PB (dashed line), PB-PMMA (solid line) and PB-PMMA-PHEMA (dotted line).

Incorporation of the methyl methacrylate and the 2-hydroxy ethyl methacrylate was confirmed by $^1$H NMR (**Figure 3**). The methoxy groups of the PMMA show a peak at 3.56 ppm and characteristic peaks for the ethyl group of PHEMA appear at 3.75 and 4 ppm. Absolute molecular weights of the PB and the PB-PMMA were measured by MALDI-TOF to determine the MMA content (70%wt for both PB$_{97}$-PMMA$_{123}$ and PB$_{60}$-PMMA$_{76}$, subscripts denote the degree of polymerization, see **Table 1**) and the composition in HEMA was determined by $^1$H NMR (PB$_{97}$-PMMA$_{123}$-PHEMA$_3$ and PB$_{60}$-PMMA$_{76}$-PHEMA$_2$). The amount of HEMA incorporated in the polymers was lower than expected. As the TMS protective groups are very sensitive, complete deproctection was assumed.
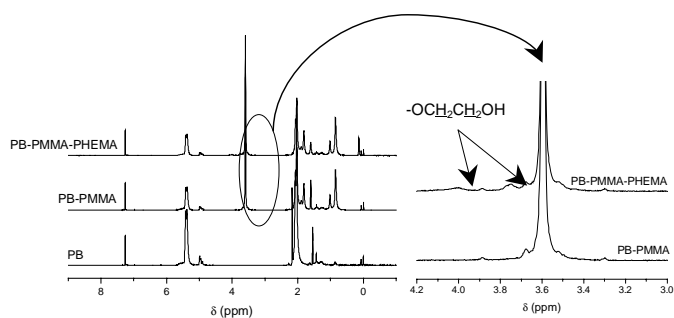
**Figure 3**. ^{1}H NMR traces showing the incorporation of both PMMA and PHEMA blocks.

**Table 1**. Block copolymers synthesized. The subscripts denote number-average degrees of polymerization.

|  | $M_w^a$ (g/mol) | $PDI^a$ |
|---|---|---|
| $PB_{97}$-$PMMA_{123}$ | 12,600 | 1.04 |
| $PB_{97}$-$PMMA_{123}$-$PHEMA_3$ | 13,100 | 1.04 |
| $PB_{60}$-$PMMA_{76}$ | 7,700 | 1.08 |
| $PB_{60}$-$PMMA_{76}$-$PHEMA_2$ | 8,100 | 1.08 |

[a]GPC, PB calibration

**Solution behaviour.** In acetone, at 1 g/L, spherical aggregates with hydrodynamic radius around 200 nm were observed in DLS for $PB_{97}$-$PMMA_{123}$ and $PB_{97}$-$PMMA_{123}$-$PHEMA_3$, indicating strong aggregation. In DMF, hydrodynamic radii of 16 and 17 nm were detected for $PB_{97}$-$PMMA_{123}$ and $PB_{97}$-$PMMA_{123}$-$PHEMA_3$, respectively. In ACN, $PB_{97}$-$PMMA_{123}$ and $PB_{97}$-$PMMA_{123}$-$PHEMA_3$ show hydrodynamic radii at 18 and 19 nm and $PB_{60}$-$PMMA_{76}$ and $PB_{60}$-$PMMA_{76}$-$PHEMA_2$ at 11 and 12 nm (**Figure 4**). These values are typical of micelles. No proper signal could be recorded for the second set of block copolymers in acetone and DMF, which might be due to the low molecular weight of the PB block (~3000 g/mol). ACN seems to be a better selective solvent compared to acetone and DMF, stabilizing the micellar structures.
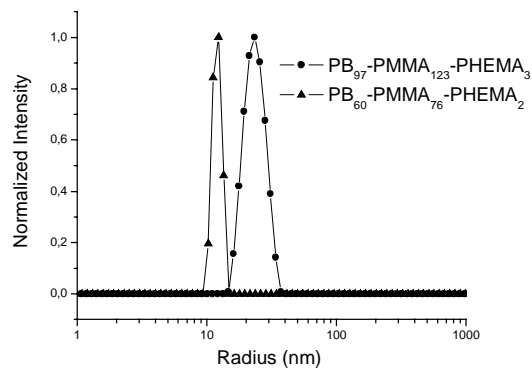


**Figure 4**. Intensity-weighted CONTIN plots for $PB_{97}$-$PMMA_{123}$-$PHEMA_3$ and $PB_{60}$-$PMMA_{76}$-$PHEMA_2$ micelles in acetonitrile.

**Crosslinking of block copolymer micelles.** $PB_{97}$-$PMMA_{123}$ and $PB_{97}$-$PMMA_{123}$-$PHEMA_3$ were cross-linked in ACN using $S_2Cl_2$. The CONTIN plots (**Figure 5**) show a narrow size distribution of the nanoparticles with a hydrodynamic radius of 17 nm (PDI = 0.3). Dialysis against the non-selective solvent THF was performed to confirm the crosslinking. Nanoparticles with a hydrodynamic radius of 19 nm (PDI = 0.2) could still be detected in THF.
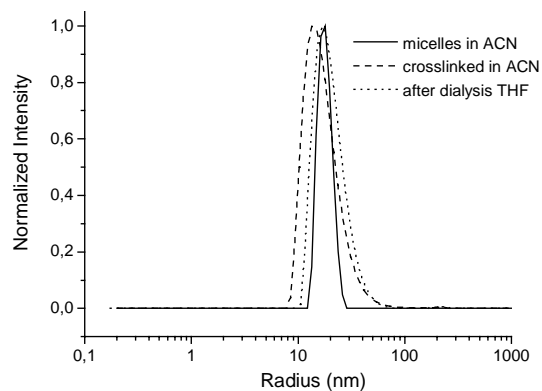


**Figure 5**. Mass-weighted CONTIN plots for $PB_{97}$-$PMMA_{123}$-$PHEMA_3$ micelles in ACN (solid line), after crosslinking ($S_2Cl_2$ 1:1) in ACN (dashed line) and after dialysis against THF (dotted line).

These measurements are confirmed by the TEM micrograph in **Figure 6**, showing spherical nanoparticles with an apparent radius around 20 nm. One can also notice that these particles are hexagonally arranged which is a sign of a very low polydispersity.
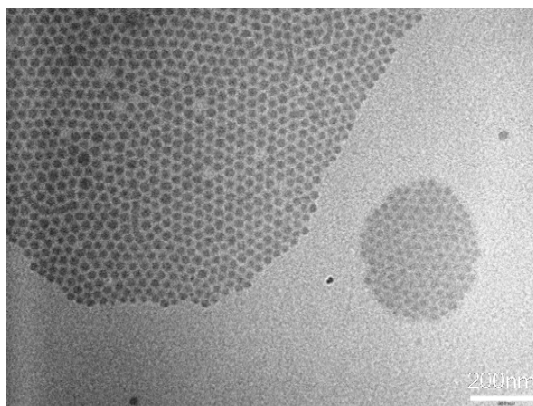


**Figure 6**. TEM image of $PB_{97}$-$PMMA_{123}$ cross-linked using $S_2Cl_2$ (1:1) in ACN. Drop-cast from 0.1g/L THF solution onto a carbon-coated grid.

**Conclusions**

Sequential anionic polymerization of butadiene-methacrylate block copolymers was successfully achieved without end-capping at room temperature in toluene. ACN proved to be the best selective solvent for micelle formation. Crosslinking of these aggregates in ACN by $S_2Cl_2$ led to narrowly distributed polymeric nanoparticles.

**References**

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