Synthetic Polymeric Nanoparticles by Nanoprecipitation

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Supporting Information

Materials and Methods

Materials

Styrene and anisole were bought from Aldrich and purified over a neutral alumina oxide column prior to use. Chloroform and methanol were obtained from Biosolve, Ltd. and were used without further purification. MAMA as an SG-1 based alkoxyamine initiator and *N*,*N*-*tert*-butyl-*N*-[1'-diethylphosphono-2-2'-dimethylpropyl] nitroxide (SG-1) as a free nitroxide were purchased from Arkema and used as received. Azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized from methanol. 2-Cyano-2-butyl dithiobenzoate (CBDB, chain transfer agent) was kindly provided by AGFA. CuBr (99.999%, Aldrich), Cu(II)Br (99.999%, Aldrich), ethyl 2-bromoisobutyate (EB*i*B) (98%, Aldrich), PMDETA (99%, Aldrich), and MMA (99%, Aldrich) were used as received. Poly(styrene), poly(methyl methacrylate), poly(ε-caprolactone), poly(vinylcarbazole), poly(styrene-*co*-acrylic acid) and poly(ethylene) are technical samples. Purified *N*,*N*-dimethylacetamide (DMA) was purchased from VWR.

Preparation of the poly(styrene) samples

Polystyrene homopolymers were prepared by nitroxide mediated polymerization. The optimum polymerization conditions, e.g. polymerization temperature and concentration of free-nitroxide, were determined in previous studies.[1] It was reported that there is no significant effect of excess free-nitroxide on the control over the polymerization of styrene. However, the polymerization temperature has a critical importance for obtaining polymers with narrow polydispersity indices. Therefore, the reactions were performed at 110 °C (PS2, PS5, and PS6) or 120 °C (PS1, PS3, and PS4) without any additional free-nitroxide.

Different ratios of styrene to Bloc Builder were used, e.g. 50:1 (PS-1), 80:1 (PS-2), 100:1 (PS-3), 150:1 (PS-4), 160:1 (PS-5), and 240:1 (PS-6), to synthesize the poly(styrene) samples. Anisole was used as solvent in all NMP reactions. The polymerization of styrene was conducted at 110 °C for 15 h or at 120 °C for 6 h, respectively. Following the polymerization, the Schlenk tube was cooled down with water and the solution was diluted with THF. The polymer was purified by precipitation twice into methanol and dried in a vacuum oven overnight. The monomer conversion for all polymerizations were determined by GC and found to be around 70%. The molar masses and PDI values of the polymers were measured by SEC and the traces are depicted in Figure 1.

Preparation of the poly(methyl methacrylate) samples

Reversible addition-fragmentation chain transfer (RAFT) polymerization of methyl methacrylate (MMA) was performed in toluene using AIBN as initiator and CBDB as chain transfer agent. All chemicals were added into a schlenk tube and bubbled with Argon for 30 min. The reaction was conducted at 70 °C for 12 h. PMMA-1 was precipitated into methanol twice to remove the unreacted monomer and solvent.

PMMA-2 was prepared via atom transfer radical polymerization (ATRP) as reported previously.[2]

Nanoparticle preparation by dialysis

In general, the polymer sample (10 mg) was dissolved in 2.5 mL DMA and dialyzed against 400 mL of distilled water. The water was exchanged five times after at least 3 h of dialysis.

Nanoparticle preparation by the dropping technique

In general, 10 mg of the polymer sample was dissolved in 2.5 mL acetone. The solution was added dropwise to 10 mL distilled water. The resulting nanoparticle suspensions were stirred at 50 °C for 10 h until the acetone was completely removed from the aqueous suspension.

Characterization of the polymers and nanoparticles

GC measurements were performed on an Interscience Trace GC with a Trace Column RTX-5 connected to a PAL autosampler. For the injection of polymerization mixtures, a special Interscience liner with additional glass wool was used. GPC was measured on a Shimadzu system equipped with a SCL-10A system controller, a LC-10AD pump, a RID-10A refractive index detector and a PL gel 5 mm Mixed-D column utilizing a chloroform:triethylamine:isopropanol (94:4:2) mixture as eluent at a flow rate of 1 mL/min and column temperature of 50 °C. The molar masses were calculated against polystyrene standards (from 3,420 g/mol to 246,000 g/mol).

The particle sizes and polydispersity indices of the nanoparticles (PDI_P) were determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Instruments, Malvern, UK). The suspensions were diluted with demineralized, filtered water to a concentration of about 0.005%. The mean particle size was approximated as the z-average diameter and the width of the distribution as the PDI_P obtained by the cumulants method assuming a spherical shape.[3] Each sample was measured for 7.5 min (corresponding to 3 runs over 150 s).

For scanning electron microscopy (SEM) studies, one droplet of the nanoparticle suspension was lyophilized on a mica surface and covered with gold. The images were obtained with a SEM LEO-1530 VP Gemini (LEO, Oberkochen, Germany) operating at 10 kV.

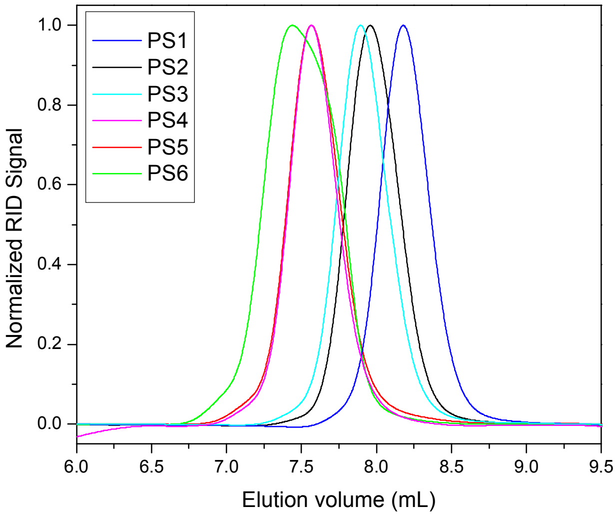

Fig 1. SEC traces of the polystyrene homopolymers.

References

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