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Low Molar Mass Poly(styrene-*co*-acrylic acid) Amphiphilic Block Copolymers: Synthesis and Characterization

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SUMMARY: Low molar mass (~ 4000) di- and triblock copolymers of styrene and tert-butyl acrylate were synthesized by atom transfer radical polymerization (ATRP) in bulk and solution conditions. A CuBr/N, N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) catalyst system in conjunction with an alkyl-halide initiator were used to control the synthesis of the polystyrene macroinitiator and the subsequent copolymerization with tert-butyl acrylate. Hydrolysis of the tert-butyl acrylate blocks to acrylic acid blocks in the presence of trifluoroacetic acid resulted in the formation of an amphiphilic block copolymer. Size exclusion chromatography (SEC) and matrix assisted laser desorption ionization - time of flight - mass spectrometry (MALDI-TOF-MS) were used to determine the molar mass and molar mass distribution of the polystyrene macroinitiators and the block copolymers. ^{1}H NMR was used to characterize the polystyrene macroinitiators and the block copolymers, and to confirm hydrolysis of the poly(tert-butyl acrylate) blocks to poly(acrylic acid).

Introduction

Block copolymers have received much attention in the last three decades. Their unique chemical structures result in physical and mechanical properties different and sometimes more advantageous than their homopolymer counterparts [1]. Their synthesis has also received much attention, since their block-like nature requires careful construction in terms of size and distribution so as to deliver the necessary characteristics [1-3]. The advent of living/controlled polymerization techniques has allowed chemists to synthesize polymers with predictable molecular masses and narrow molecular mass distributions. Atom transfer radical polymerization (ATRP) is one such controlled synthesis process and its application in block copolymer synthesis is invaluable [4,5]. Amphiphilic block copolymers inherently have the ability to act as surfactants due to their dual activity of hydrophilicity and hydrophobicity and have been used in emulsion polymerizations [6] and particle dispersions [7-9].

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The poly(styrene-co-tert-butyl acrylate) block copolymers were synthesized via copper-mediated ATRP in conjunction with an alkyl-halide initiator [10,11]. Hydrolysis of the tert-butyl acrylate blocks to acrylic acid blocks in the presence of trifluoroacetic acid resulted in the formation of an amphiphilic block copolymer [6].

Experimental

Materials

Styrene (Aldrich, 99%) was dried overnight with anhydrous CaH_2 (Aldrich, 90-95%) and thereafter distilled under vacuum at 60°C. Tert-butyl acrylate (tBA, Aldrich, 98%) was extracted three times with an equal volume of 5% aqueous NaOH (BDH, 99%, pellets) and subsequently washed once with an equal volume of distilled water. It was dried with anhydrous $CaCl_2$ (Unilab, 4-8 mesh) and distilled under vacuum at 60°C. Bromoethylbenzene (BEB, Aldrich, 97%), dimethyl-2,6-dibromoheptanedioate (DMDBHD, Aldrich, 97%), N, N, N', N'', N'' – pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), CuBr (Aldrich, 98%) and trifluoroacetic acid (TFA, BDH, 99%) were all used as received.

Macroinitiator synthesis

Polystyrene mono-functional macroinitiators with molecular masses of ~1000, ~2000 and ~3000 were synthesized. One di-functional polystyrene macroinitiator of ~2000 molecular mass was also synthesized.

CuBr, styrene and PMDETA were added to a dry Schlenk flask and stirred to form the Cu/ligand complex. The complexation is complete when the solution turns from colourless to green. The addition of a solvent such as acetone was optional and it was dependent on the viscosity of the reaction mixture and the ability for adequate mixing to take place. The BEB (mono-functional initiator) or DMDBHD (di-functional initiator) was then added and the flask was sealed with a rubber septum. The contents of the flask was subjected to three freeze-thaw cycles under vacuum to remove oxygen from the reaction mixture and then left under nitrogen. The freeze-thaw cycles needed to be carried out immediately after initiator addition to minimize the probability of oxygen interfering with the initiation step. The reaction was allowed run overnight. It was then dissolved in acetone and filtered through alumina to remove the copper catalyst from the polymer. The acetone was removed by evaporation under vacuum and the polymer was redissolved in a minimum volume of diethyl ether. The polymer was precipitated from methanol and vacuum dried to yield a powder.

Block copolymer synthesis

The polystyrene macroinitiators were used to initiate the growth of the tert-butyl acrylate (tBA) blocks. However, it must be noted that for the di-functional initiator there are two moles of initiation sites per one mole of polystyrene macroinitiator. The synthesis and purification was carried out as for the macroinitiator, but the block copolymer was precipitated from a 50:50 (v:v) water/methanol mixture.

Hydrolysis

The poly(tert-butyl acrylate) blocks were hydrolysed to poly(acrylic acid) in the presence of TFA catalyst in dichloromethane at room temperature after 24 hours. The solvent was evaporated under vacuum and the polymer was vacuum dried.

Analytical techniques

The molecular mass and molecular mass distributions were determined by SEC using tetrahydrofuran as eluent, a phenogel column (500Å pore size, 3000 x 7.8 mm), a refractive index detector and polystyrene standards. A 2,5-dihydroxybenzoic acid matrix was used in the MALDI-TOF-MS (Voyager-DE STR) analysis. No salt solution was added to charge the samples as it was observed that sodium (from the glassware) and copper (from the metal halide catalyst), inherently present in the polymer, provided sufficient charging. The matrix and polymer were premixed in a 4:1 ratio (concentrations of 40 mg/ml and 2,6 mg/ml in tetrahydrofuran (THF), respectively). The polymers were characterized by ^{1}H NMR using a 300 MHz Bruker ARX300 spectrometer. Deuterated trichloromethane was used as the solvent for the polystyrene macroinitiators and the unhydrolysed block copolymers. Deuterated dimethylsulphoxide was used as the solvent for the hydrolysed block copolymers.

Results and Discussion

Table 1 gives a detailed description of the amounts of reactants used for each macroinitiator synthesis and SEC and MALDI-TOF-MS results.

Table 1 Reagent ratios for polystyrene macroinitiator synthesis via ATRP and SEC and MALDI-TOF-MS results.

				SEC[●]		**MALDI-TOF-MS[●●]**	
Experiment[#]	**M:I:Cu:L[*]**	**Solvent**	**Mn (theo)[x]**	**Mn (exp)**	**PDI[%]**	**Mn (exp)**	**PDI[%]**
1PstA	21:1:0.2:0.2	Bulk	2000	2072	1.21	2277	1.09
1PStC	13:1:0.1:0.1	Bulk	1000	1510	1.06	1659	1.06
1PStD	10:1:2:0.2	Bulk	3000	2510	1.26	2841	1.05
1PstE	29:1:0.2:0.2	Bulk	1000	1652	1.09	1693	1.07
1PStF	11:1:0.2:0.2	Bulk	3000	3016	1.13	3093	1.04
2PStB	29:1:0.2:0.2	Bulk	2000	2333	1.10	2448	1.07

[●] Size Exclusion Chromatography – Polystyrene standard, THF solvent

[●●] Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry

[#] The first digit is associated with the number of functionalities on the macroinitiator

[*] Molar ratios: styrene monomer (M), initiator (I), CuBr catalyst (Cu) & PMDETA ligand (L)

[x] Molecular mass calculated by: M_n (theo) = gram monomer/mol initiator

[%] Polydispersity index

The data given in Table 1, show that the polystyrene macroinitiators were reliably synthesized via ATRP. The molecular masses and molecular mass distributions obtained were satisfactory, relative to the values required.

Table 2 gives a detailed description of the amounts of reactants used for each block copolymer synthesis.

Table 2 Reagent ratios for poly(styrene-co-tert-butyl acrylate) block copolymer synthesis via ATRP and SEC and MALDI-TOF MS results thereof.

					SEC[●]		MALDI-TOF MS[●●]	
Experiment[#]	**Initiator**	**M:I:Cu:L***	**Solvent[@]**	**Mn (theo)[x]**	**Mn (exp)**	**PDI[%]**	**Mn (exp)**	**PDI[%]**
1PSt-P(tBA)A	1PStA	20:1:0.5:0.5	25%	4000	4251	1.28	4396	1.34
2P(tBA)-PSt-P(tBA)B	2PStB	20:1:0.5:0.5	25%	4000	4375	1.76	4342	1.30
1PSt-P(tBA)C	1PStC	20:1:0.5:0.5	26%	4000	3783	1.18	3814	1.24
1PSt-P(tBA)D	1PStD	12:1:0.5:0.5	24%	4000	4090	1.17	3947	1.29
1PSt-P(tBA)E	1PStE	13:1:0.3:0.3	26%	4000	3014	1.11	3540	1.24
1PSt-P(tBA)F	1PStF	15:1:0.6:0.6	24%	4000	4078	1.10	3997	1.29

[●] Size Exclusion Chromatography – Polystyrene standard, THF solvent

[●●] Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry

[#] The first digit is associated with the number of functionalities on the macroinitiator

* Molar ratios: tert-butyl acrylate monomer (M), polystyrene macroinitiator (I), CuBr catalyst (Cu) and PMDETA ligand (L)

[@] Volume percent acetone relative to tert-butyl acrylate monomer

[x] Molecular mass calculated by: M_n (theo) = gram monomer/mol initiator

[%] Polydispersity index

As with the polystyrene macroinitiators the block copolymers showed satisfactory results with respect to molecular mass and molecular masses distributions. The ^{1}H NMR spectrum of the hydrolysed block copolymer shows the disappearance of the dominant resonance peak at 1.4 ppm (Figure 1), due to the protons of the tert-butyl group, that was observed for all the poly(styrene-co-acrylic acid) block copolymers. Figure 2 shows the ^{1}H NMR spectrum of the hydrolysed block copolymer.

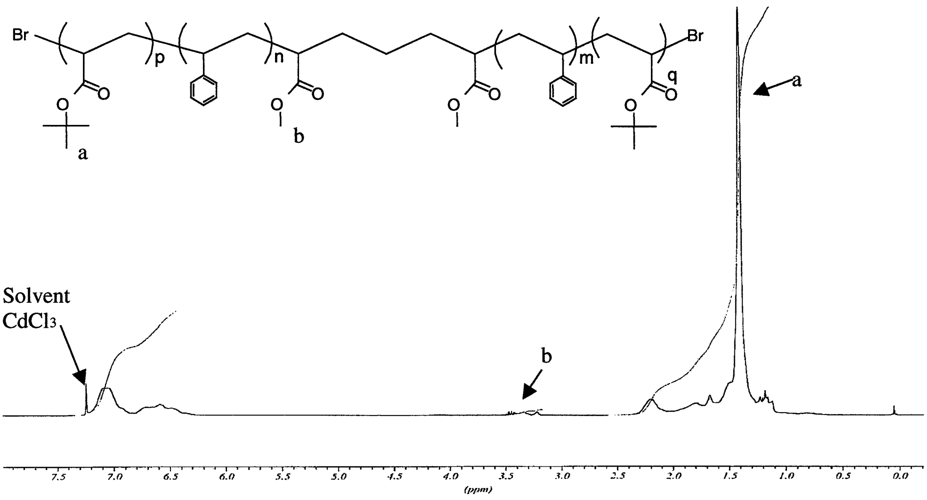

Fig. 1 ^{1}H NMR spectrum of the poly(styrene-co-tert-butyl acrylate) tri-block copolymer showing the dominant peak at 1,4 ppm due to the tert-butyl acrylate protons.

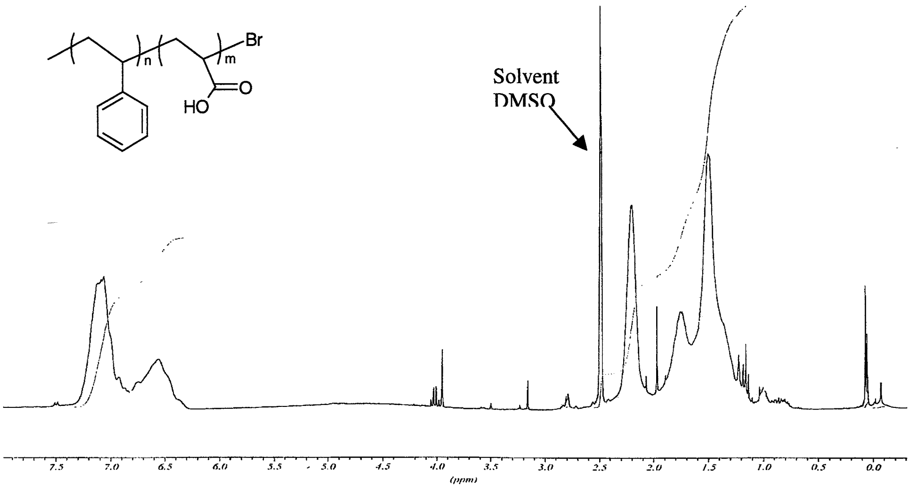

Fig. 2 ^{1}H NMR spectrum of the poly(styrene-co-acrylic acid) tri-block copolymer showing the elimination of the tert-butyl acrylate peak upon hydrolysis. Peaks from 1,0 – 2,5 ppm are representative of the backbone protons. The large peak at 2,5 ppm is the deuterated dimethylsulphoxide solvent.

1. I. Pirma, *Polymeric Surfactants,* Marcel Dekker Inc., New York, (1992).
2. A. Noshay and J.E. McGrath, *Block Copolymers: Overview and Critical Survey,* Academic Press, Inc., New York, (1977).
3. E. Franta and P.F. Rempp, Chemtech, January, 24, (1996).
4. K. Matyjaszewski, *Overview: Fundamentals of controlled /living radical polymerization,* Controlled Radical Polymerization, American Chemical Society, Washington D.C., (1998).
5. K. Matyjaszewski, *Mechanistic aspects of atom transfer radical polymerization,* Controlled Radical Polymerization, American Chemical Society, Washington D.C., (1998).
6. C. Burguière, S. Pascual, B. Coutin, A. Polton, M. Tardi, B. Charleux, K. Matyjaszewski and J.P. Vairon, Macromolecular Symposia, *150,* 39-44, (2000).
7. V.I. Shvets, V.V. Karpov and E.V. Popov, Kollodnyi Zhurnal, *49,* (1), 104-109, (1987).
8. C. Poncet-Legrand, F. Lafuma and R. Audebert, Colloids and Surfaces A: Physicochemical and Enginnering Aspects, *152,* 251-261, (1999).
9. F.L. Duivenvoorde, C.F. van Nostrum, J. Laven and R. van der Linde, Journal of Coatings Technology, *72,* (909), 145-152, (2000).
10. K.A. Davis and K. Matyjaszewski, Macromolecules, *33*, 4039-4047, (2000).
11. K.A. Davis, B. Charleux and K. Matyjaszewski, Journal of Polymer Science: Part A: Polymer Chemistry, *38*, 2274-2283, (2000).