The Synthesis of Densely Grafted Copolymers by Atom Transfer Radical Polymerization

Kathryn L. Beers, Scott G. Gaynor, and Krzysztof Matyjaszewski*

Department of Chemistry, Mellon Institute, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Sergei S. Sheiko and Martin Möller*

*University of Ulm, Organishe Chemie III/ Makromolekulare Chemie, 89069 Ulm, Germany*

Recent progress in the field of densely grafted, or "brush" (co)polymers has prompted a need to develop efficient methods to synthesize a wider variety of materials with the same basic architectural design. These brushlike macromolecules have been prepared previously using the macromonomer method.[1−6] Macromonomers, usually prepared by anionic polymerization, were homopolymerized using conventional radical methods to maximize the number of branches possible from a linear backbone based on vinyl monomers. Upon fractionation of these materials using size exclusion chromatography, samples of narrow polydispersities were obtained which could then be cast on surfaces to form highly ordered thin films. To avoid the rigorous methods necessary for ionic polymerizations and sample fractionation, and to extend the variety of compositional content of these types of materials, atom transfer radical polymerization (ATRP) has been used to prepare similar macromolecular architectures.

The approach described here involves grafting from a macroinitiator and can offer greater versatility in terms of both the length and the composition of the backbone and/or the side chains than previous methods which employed the synthesis of high molecular weight macromonomers and their subsequent polymerization by uncontrolled radical techniques; to obtain well-defined polymeric brushes required their fractionation, generally by SEC. To our knowledge, there are no known examples of using a macroinitaitor with a grafting site at each repeat unit to make well-defined polymeric brushes.

Combinations of nitroxide-mediated, conventional free radical polymerization and ATRP to prepare graft copolymers from macroinitiators have been used previously.[7,8] ATRP has also been combined with conventional radical polymerization to prepare amphiphilic graft copolymers[9] and thermoplastic elastomers,[10] as well. In each of these cases, however, the materials are loosely grafted, having been prepared from a macroinitiator which is a copolymer containing both initiation/ branch sites and spacing repeat units.

Controlled radical polymerization and ATRP in particular afford access to materials of controlled molecular weight, predicted by the ratio of consumed monomer to initiation sites.[11,12] This method also yields polymer segments of narrow molecular weight distributions[13] in addition to being applicable to a host of vinyl monomers such as styrene, (meth)acrylates, acrylonitrile, etc.[14] Thus, there are many possibilities which make its application to the area of brush (co)polymers appealing.
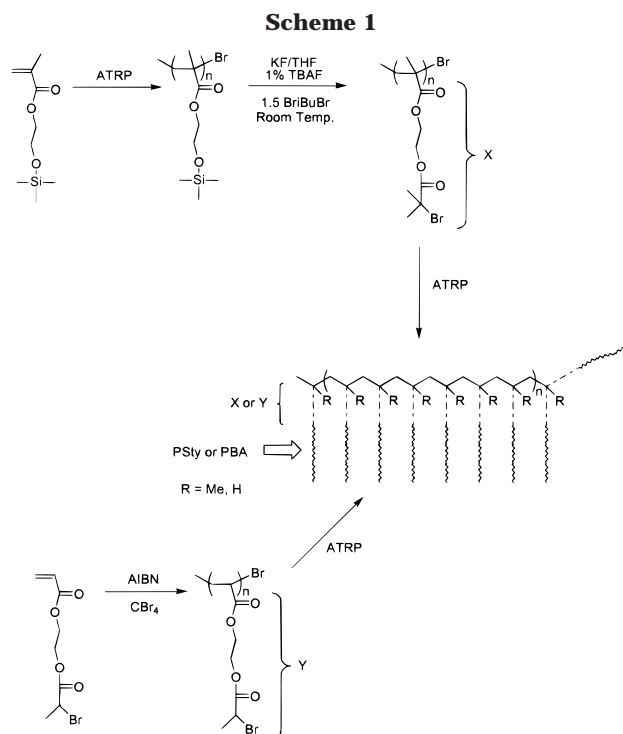
Scheme 1

Included here are preliminary synthetic data and AFM images which show that it is possible to prepare densely grafted copolymers using ATRP.

Two approaches were used to prepare the macroinitiators, Scheme 1. The first involved conventional free radical homopolymerization of 2-(2-bromopropionyloxy)-ethyl acrylate (BPEA)[15] using AIBN in the presence of carbon tetrabromide to attenuate the molecular weight (M_n = 27 300, M_w/M_n = 2.3). By use of AIBN as an intiator to prepare the ATRP macroinitiator, a polymer with a broad molecular weight distribution was obtained. Such a macroinitiator would consequently result in the formation of brush polymers with broad molecular weight distributions, no matter how well controlled the polymerization of the side chains.

Thus, the preparation of a well-defined macroinitiator was undertaken. In the second approach, trimethylsilyl-protected 2-hydroxyethyl methacrylate (HEMA-TMS)[16] was polymerized via ATRP and subsequently esterified with 2-bromoisobutyryl bromide (BriBuBr) in the presence of a catalytic amount of tetrabutylammonium fluoride (TBAF) to yield a different macroinitiator, poly-(2-(2-bromoisobutyryloxy)ethyl methacrylate) (pBIEM)[16] with controlled molecular weight and low polydispersity (M_n = 55 500, M_w/M_n = 1.3), Table 1. It should be noted that the macroinitiator prepared using ATRP was composed of a stiffer methacrylate structure and with a 2-bromoisobutyryl initiation site while the free radically prepared pBPEA contained an acrylate backbone and 2-bromopropionyl initiation sites. However, both types of initiating species have been shown to initiate styrene polymerization well.[14]

Both polymers were then used as macroinitiators for ATRP of styrene (S) and butyl acrylate (BA). Side chains with a degree of polymerization of about 40 from a macroinitiator of pBIEM with a M_n of approximately 50 000 (which contained about 200 initiation sites per

Table 1. Molecular Weight Data for Macroinitiators and Graft Copolymers ("Linear" and "Triple Det" Correspond to Linear Polystyrene Standards and Triple Detection Used for GPC Data Analysis, Respectively)

	free radical pBPEA			pBIEM via ATRP		
	M_n	M_w/M_n			M_n	M_w/M_n
pBPEA	27,300 (linear)	2.3	pBIEM		55 500 (linear)	1.3
graft copolymer (styrene grafts)	34 200 (linear)	3.2	graft copolymer (styrene grafts)		175 000 (linear)	1.39
	90 800 (triple det)	2.2			4 980 000 (triple det)	1.2

Table 2. Reaction Conditions for ATRP Of Styrene and Butyl Acrylate from P(BIEM) (All Values Related to Molecular Weight Based on Refractive Index Detection Calibrated vs Linear Polystyrene Standards)

num	M	[M]:[I]^a:[Cu(I)]: [Cu(II)]:[dNbpy]	temp (°C)	time (h)	target conv (%)	conv (%)	$M_n(M_w/M_n)$ P(BIEM)	graft copolymer
1	S	320:4:1:0.04:2	110	6	50	>80	9 300 (1.19)	204 000 (5.0)^c
2	S	100:1:0.1:0:2	90	5	50	< 15	9 300 (1.19)	349 000 (4.9)^c
3	S	200:1:0.1:0:2	80	45	25	N/A	55 500 (1.3)	216 000 (1.6)^c
4	S		60	264	25	none	55 500 (1.3)	N/A
5	S	400:1:0.4:0.03:0.8	80	3	12.5	13	55 500 (1.3)	237 000 (1.31)
6	S		70	72	12.5	30^b	55 500 (1.3)	187 000 (1.39)
7	S		70	18	12.5	13	20 700 (1.23)	88 700 (1.21)
8	BA	400:1:0.5:0.026:1	80	4	12.5	14	9 300 (1.19)	91 600 (1.15)
9	BA		70	7	12.5	12	55 500 (1.3)	271 000 (1.38)

^{a} [I] is defined as the molar amount of Br in the macroinitiator assuming complete transformation of the polymer (mass of sample/ molecular weight of BIEM). ^{b} Due to the long reaction time necessary, some of this loss of monomer is attributed to absorption into and/or through the rubber septa. ^{c} Measured from soluble fraction only.
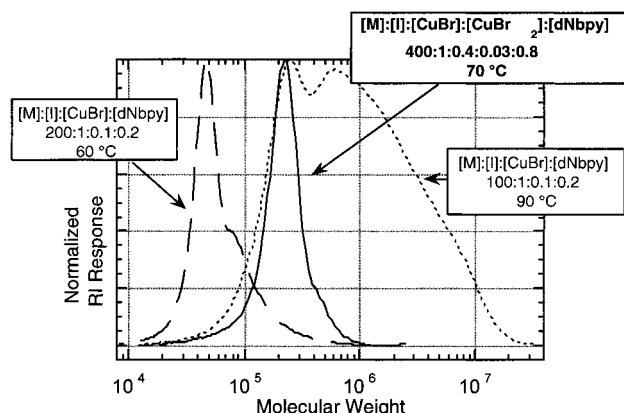
Figure 1. GPC traces of dense graft copolymers prepared via ATRP under various reaction conditions (calibrated vs linear polystyrene standards). All reactions done in bulk with temperatures and conditions shown.

chain) were targeted in order to construct molecules which would be sufficiently stiffened and elongated by the steric bulk of the side chains and thus assume an extended rodlike structure when cast on a surface.[17] However, grafting from the macroinitiators with a high density of initiation sites was more complicated than the traditional ATRP of styrene discussed previously.[11−13,18]

One consequence of using radical polymerization to grow the side chains from the backbone is that radical−radical coupling must be significantly suppressed; otherwise, cross-linked polymers or polymers with multimodal molecular weight distributions may result (cf. entries 1−3, Table 2). To avoid this, various conditions of the polymerization including temperature and catalyst and initiator concentrations were optimized to prevent as much termination during polymerization as possible. Examples of resulting SEC traces of graft copolymers obtained under a few different reaction conditions are shown in Figure 1. The molecular weights of these polymers were determined using a calibration curve based on linear polystyrene standards, and as such, the values obtained for the polymeric brushes are, in all likelihood, severely underestimated. As a qualitative analysis of the success of the polymerization, however, we evaluated the shape of the SEC traces: broad or multimodal distributions would be indicative of side reactions of the growing side chains, i.e., termination, while narrow molecular weight distributions which were of higher molecular weight than the starting macroinitiator would suggest that undesirable side reactions in the polymerization were minimized.

To suppress termination reactions the polymerization of the side chains were conducted in bulk monomer, but under dilute conditions. To obtain the desired length of the side chains, the polymerization had to be stopped at low conversions: usually between 10 and 20%. Table 2 lists a series of experiments using well-defined pBIEM as the macroinitiator for different reaction conditions in the polymerization of S or BA. For successful synthesis, $Cu^{II}Br_2$ was added to avoid its spontaneous formation in situ by radical termination. This established better control by anticipation of the persistent radical effect.[19] Lower temperatures and lower [Cu(I)] were also used to reduce the concentration of radicals during polymerization.

Due to the high density of branches in these materials, SEC data analysis using refractive index detection calibrated vs linear polystyrene standards does not yield accurate molecular weight data. SEC with on-line viscometry and light scattering detection (3D-SEC) was therefore used to provide a more accurate estimate of molecular weight and polydispersities. Results from these experiments are listed in Table 1. The values for dn/dc used were based on the composition of the side chains since they comprised the bulk of the material (> 95%). As can be seen, the increase in molecular weight from the macroinitiator is more dramatic when the 3D-SEC was used. Although this increase in molecular weight, as well as examination of the ^1H NMR spectra,[16] suggests that the brushes were formed at all initiating sites (within the experimental error of NMR), clearer evidence is found when these polymers are examined by atomic force microscopy (AFM).

Films were cast on mica from a toluene solution (0.01 wt %) of the resulting graft copolymers and images of the polymers were obtained by AFM without any sample
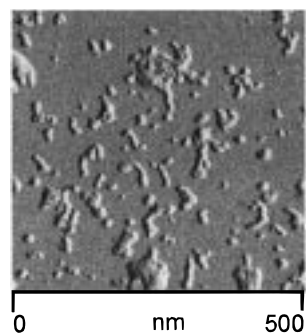
Figure 2. AFM images of dense graft copolymers. Polystyrene grafted from ill-defined macroinitiator, pBPEA: M_n =27 300; M_w/M_n = 2.3.
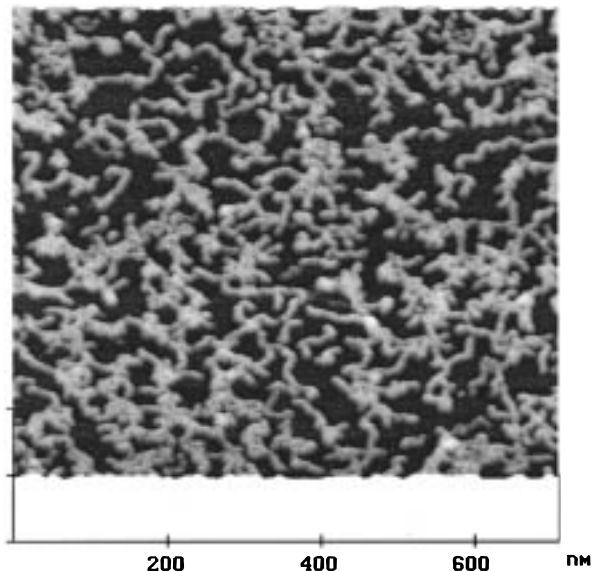

Figure 3. AFM images of dense graft copolymers. Polystyrene grafted from well-defined macroinitiator, pBIEM: M_n = 55 500; M_w/M_n = 1.3.

fractionation. As can be directly seen in Figures 2 and 3, the distribution of chain lengths obtained using the conventional free radically prepared macroinitiator (Figure 2) is much broader than those prepared from macroinitiators of controlled molecular weights (Figure 3), although the molecular cross-sectional areas from the two samples are similar. The polymeric brushes prepared using entirely ATRP are on average 100 nm long, 10 nm wide, and 2 nm high. The asymmetric cross-sectional dimensions are due to the collapse of the polymer chains onto, and the interaction with, the surface after removal of solvent.

Thus, densely grafted, brush copolymers can be synthesized using atom transfer radical polymerization to obtain well-defined molecules which can be imaged and whose dimensions can be visualized by AFM. It should be noted that in order to obtain well-defined polymers, with a minimization of side reactions, the reaction conditions must be optimized. These conditions include temperature, and varying the concentration of all reagents: macroinitiator, monomer, catalyst (Cu^{I}Br), and deactivator (Cu^{II}Br$_2$). Future work includes the optimization of these conditions for a variety of monomers, functionalization of the side chain end groups and the synthesis of block copolymers, both in the side chains and in the backbones.

Supporting Information Available: Text giving details of polymer synthesis and figures showing ^{1}H NMR spectra of the macroinitiator and the brush polymers (6 pages). Ordering and Internet access information is given on any current masthead page.

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