Graft Copolymers by Atom Transfer Polymerization

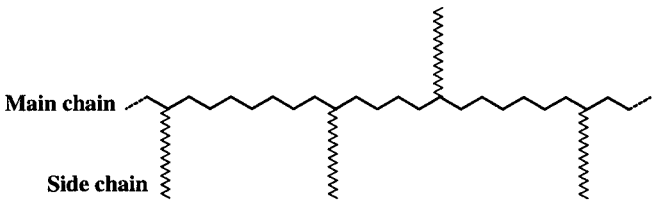
*Hans G. Börner and Krzysztof Matyjaszewski**

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA

Summary: Various graft copolymers have been prepared by atom transfer radical polymerization (ATRP) using both "grafting through" and "grafting from" approaches. The synthesis and some properties are reviewed.

Introduction

Graft copolymers represent valuable polymeric materials, since a variety of molecular parameters can be varied (as shown in Scheme 1): i) main and side chain polymer type, ii) degree of polymerization and polydispersities of main and side chain, iii) graft density (average spacing in-between the side chains) and iv) distribution of the grafts (graft uniformity). Using special polymerization techniques tailor-made graft copolymers can be afforded according to specific needs.



Scheme 1: Graft copolymer.

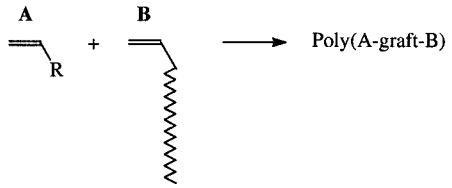
By controlling the molecular parameters, one can obtain impact resistant materials by combining a hard polymer backbone with soft polymer side chains; thermoplastic elastomers, where a soft polymer backbone is grafted with hard polymer segments; or amphiphilic copolymers for applications as hydrogels, stabilizers, surface-modifying agents, dispersants, emulsifiers and compatibilizers in polymer blends, etc.[1,2].

 CCC 1022-1360/00/$ 17.50+.50/0

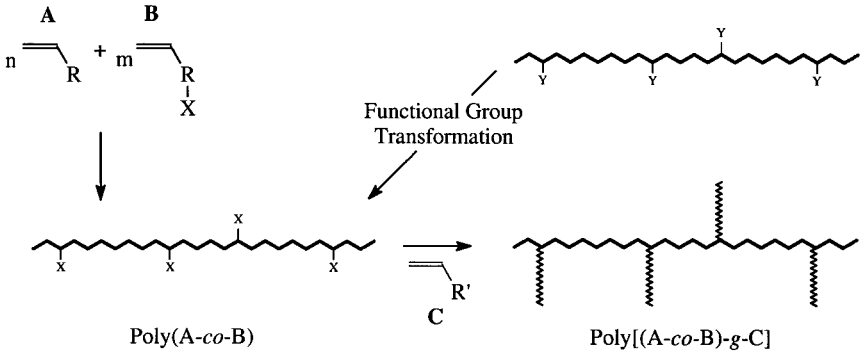
Three main methods can be used to prepare graft copolymers: i) "grafting through", where a macromonomer is copolymerized with a low molecular weight comonomer; ii) "grafting from"; in this case a macroinitiator with predetermined initiation sides is used to initiate the polymerization of a second monomer; iii) "grafting onto", where an end-functional or a living polymer with reactive end-group is coupled with functional groups located on another polymer.

Until recently, well-defined graft copolymers could be obtained only by using ionic polymerizations or the macromonomer route. Due to the lack of control of molecular weight and polydispersity, the free-radical polymerization methods (FRP) lead to poorly defined polymers, very often accompanied by a certain amount of homopolymer and crosslinked material[1,3]. Free-radical techniques though have become available for the preparation of well-defined polymers. The most important types of controlled/"living" radical polymerizations are: i) stable free radical polymerization (SFRP), which usually employs nitroxyl radicals[4,5]; ii) atom transfer radical polymerization (ATRP), where complexes of transition metals such as copper[6,7], ruthenium[8], iron[9,10] or nickel[11,12], are utilized in conjunction with alkyl halides; iii) reversible addition-fragmentation chain transfer polymerization (RAFT), where dithioesters coupled with a free radical initiator induce polymerization[13]. So far only SFRP[14] and ATRP[15] have been used to prepare graft copolymers by both "grafting through" and "grafting from" methods.

ATRP has been applied in the synthesis of several well-defined graft copolymers. Two main approaches have been adapted: i) the "grafting through" technique, i.e. a well-defined macromonomer was synthesized in the first step by ATRP, followed by its free-radical or controlled radical copolymerization with a low molecular weight comonomer (Scheme 2); ii) the "grafting from" technique, i.e. a polymer possessing ATRP-active halide atoms as side groups was used as a macroinitiator in the ATRP of a second monomer. Generally, these macroinitiators can be obtained directly by copolymerizing a monomer containing ATRP-initiator group using a polymerization mechanism that is different from ATRP (FRP, SFRP, ring opening polymerization (ROMP)) or by copolymerization of a monomer carrying a precursor group that can be transformed to an ATRP-initiating group (Scheme 3).



Scheme 2: "Grafting through" approach.



Scheme 3: "Grafting from" approach.

The present paper gives an overview over the graft copolymer materials prepared by copper-mediated ATRP.

1 Graft copolymers by the "grafting through" approach

The "grafting through" approach is the most common route to controlled graft copolymers[16,17]. The copolymerization of macromonomers (MM) with low molecular weight comonomer allows good control of the polymer side chain parameters (DP, M_w/M_n) by using living or controlled polymerization methods for the MM synthesis. The polymer main chain parameters (DP, M_w/M_n) can be controlled by a living copolymerization of the MM with a low molecular weight comonomer. The average side chain density is determined by the reactivity ratio of the MM in the copolymerization and by the ratio of the MM in the feed. The spacing distribution of the side chains is the most crucial parameter to control[18]. It is influenced by the diffusion differences of MM in comparison to the low molecular weight comonomer[19], by the inherent reactivity of MM and comonomer[20] and by the potential incompatibility of the side chain polymer with the main chain polymer[21].

1.1 Poly(N-vinyl pyrrolidinone-*graft*-styrene)[22]

Well defined polystyrene macromonomers (pS-MM) were prepared initially, by ATRP using vinyl chloroacetate as initiator and $Cu[dNbpy]_2Cl$ as catalyst (dNbpy: 4,4'-Di(5-nonyl)-2,2'-bipyridine). The low reactivity of the styryl radical for the double bond of vinyl acetate suppresses its incorporation into the polystyrene chain. In this way vinyl acetate end-functionalized pS-MM was obtained having low polydispersity, high functionality and controllable molecular weight (M_n = 5800 (M_w/M_n = 1.12); M_n = 11,900 (M_w/M_n = 1.15); M_n = 15,900 (M_w/M_n = 1.18)). These MMs were copolymerized with N-vinylpyrrolidinone (NVP) using conventional radical polymerization with AIBN as initiator in DMF as solvent for both main and side chain polymer. The amount of incorporated MM (average graft density) depends on the MM ratio in the feed, but also on the MM length (decrease in graft density with increase in M_n (MM) by constant feed ratio) (Table 1). The synthesized material can be described as a thermoplastic hydrogel. It follows the concept of thermoplastic elastomers, since the hydrophilic pNVP main chains are swellable in polar solvents (e.g. water) and lead to hydrogel formations. Dissolution in water is prevented by the physically crosslinked, hydrophobic pS side chains. Microphase separation was confirmed by differential scanning calorimetry (DSC) analysis since two glass transition temperatures can be observed (e.g. $T_{g,1}$ = 74.79 (pNVP); $T_{g,2}$ = 111.3 (pS); Sample Table 1, entry 4).

Table 1: Synthesis of poly(N-vinyl pyrrolidinone-*graft*-styrene).

pS-MM M_n (M_w/M_n)	MM $_{incorporated}$ w% (feed)	Copolymer M_n (M_w/M_n)	Grafts / Chain	Equal. Content of water (%)
	34 (40)	316000 (5.90)	18.6	85
5800 (1.12)	13 (20)	219000 (2.50)	4.9	92
	8 (10)	185000 (1.80)	2.5	97
11900 (1.15)	40 (50)	65700 (1.58)	2.2	82

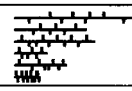
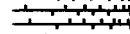
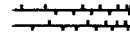
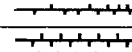
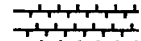
1.2 Poly(methyl methacrylate-*graft*-dimethylsiloxane) [21]

The polydimethylsiloxane (PDMS) macromonomer was synthesized by anionic ring-opening polymerization and subsequently end-functionalized with 3-methacryloxypropyl-dimethylchlorosilane (PDMS-MA: M_n = 2370; M_w/M_n = 1.25; F = 1.0)[23]. The macromonomer was copolymerized with methyl methacrylate employing various polymerization mechanisms like FRP, RAFT and ATRP under diverse

conditions (Table 2). The inverse reactivity ratio which is the reciprocal value of $r_{(comonomer)}$ as determined by Jaacks method[24] is equivalent to the relative reactivity of the MM ($1/r_{(comomomer)}$ = k(comonomer-MM)/ k(comonomer-comonomer)). $1/r_{MMA}$ was estimated in order to gain some insight about the side chain distribution in the synthesized graft copolymer.

The copolymer synthesized by conventional free radical polymerization (FRP) shows a first order heterogeneity; i.e. the chemical composition of different polymer molecules is different. This can be attributed to the short lifetime of the active growing polymer chain (~ s) and the shift of comonomer feed by faster incorporation of the low molecular weight comonomer, as indicated by the reactivity ratio of $1/r_{MMA} = 0.34$ (Table 2, entry 1). Using RAFT or ATRP, all chains grew simultaneously with the same chemical composition. According to the reactivity ratio ($1/r_{MMA} \neq 1$) the feed changes during polymerization. This results in polymers having chains of constant chemical composition, but a heterogeneous composition along each polymer chain is evident; i.e. the so-called second order heterogeneity is apparent. The obtained graft copolymer showed a gradient in side chain density (Table 2, entry 2-5). Using ATRP with a PDMS-BiB macroinitiator in semi-bulk conditions the reactivity ratio approached the ideal inverse reactivity ratio of 1. This indicates incorporation of both macromonomer and comonomer with comparable ratios and control over side chain distribution.

Table 2: Synthesis of poly(methyl methacrylate-*graft*-dimethylsiloxane).

		Conditions	Xylene (w%)	$1/r_{MMA}$ [a]	Distribution
1	FRP	[1] AIBN	31	0.34	
2	RAFT	[1,2] BPO	31	0.67	
3	RAFT	[1,2] AIBN	31	0.57	
4	ATRP	[1,3] EBiB, 75°C	31	0.73	
5	ATRP	[1,3] EBiB, 90°C	31	0.81	
6	ATRP	[1, 3] PDMS-BiB	3	0.85	

[1] MMA : PDMS-MA = 95 mol% : 5 mol%
[2] M : Cumyl dithiobenzoate : I = 300 : 1 : 0.5
[3] M : $Cu[dNbpy]_2Cl$: In = 300 : 1 : 1
[a] determined by Jaacks method[24].

1.3 Poly(methyl methacrylate-*graft*-lactide)[20]

Two different well-defined polylactide (pLA) macromonomers were prepared using hydroxyethyl methacrylate (MA) or hydroxyethyl acrylate (A) as initiator in the anionic ring-opening polymerization of lactide (pLA-MA, pLA-A; Table 3).

Table 3: PLA-Macromonomers.

	M_n +	M_w/M_n +	Functionality
pLA-MA	2800	1.16	1.0
pLA-A	2700	1.22	0.99

+ determined by GPC (THF; pMMA-standards)

The pLA-macromonomers were copolymerized with methyl methacrylate using ATRP. Since the slow ATRP reaction makes the diffusion control effect negligible and the polylactide side chains are compatible with the pMMA main chain, the reactivity of the MM is mainly determined by the inherent reactivity of the head group. The strong dependence of the reactivity ratio on the head group of the MM is shown in Table 4. The copolymerization of the oxyethylene methacrylate terminated MM (pLA-MA) with MMA results in a reactivity ratio of $1/r_{MMA} = 1.85$. On the other hand, $1/r_{MMA} = 0.61$ can be determined in the copolymerization of oxyethylene acrylate terminated MM (pLA-A) with MMA. Control over the side chain distribution can be achieved by polymerizing a mixture of both pLA-MA and pLA-A in a 50 : 50 w% ratio. The determined inverse reactivity ratio $1/r_{MMA} = 0.93$ is close to the ideal value of 1 and indicates a MM and comonomer incorporation in the polymer with comparable ratios. Furthermore, the obtained graft copolymer showed a molecular weight of $M_n = 55{,}000$, a low polydispersity index ($M_w/M_n = 1.16$), and in average 3.5 grafts per 100 MMA repeat units.

Table 4: Copolymerization of pLA-MM with MMA.

Comonomers [a)]	$1/r_{MMA}$ [b)]
MMA + pLA-MA*	1.85
MMA + pLA-A**	0.61
MMA + 0.5×pLA-MA* + 0.5×pLA-A**	0.93

a) Conditions: xylene : diphenylether = 1 : 1; 90 °C; $Cu[dNBpy]_2Cl$; 3.5 mol% MM
M : In : Cat = 300 : 1 : 1; 90% monomer conversion (GC).

b) determined by Jaacks method[24].

* oxyethyl methacrylate head group.

** oxyethyl acrylate head group.

1.4 Poly(*n*-butyl acrylate-*graft*-methyl methacrylate)[25,26]

The copolymerization of methacryloyl end-functionalized poly(methyl methacrylate) macromonomer (pMMA-MM) obtained by GTP[3,19] with *n*-butyl acrylate was elucidated by comparing FRP and ATRP as two different polymerization mechanisms.

Model studies were followed, to determine differences in reactivity ratios of low molecular weight MMA and *n*-BuA. The determined reactivity ratios in the copolymerization of MMA with *n*-BuA were similar in both conventional and controlled radical polymerizations. This indicates that the selectivity of the corresponding radicals is independent of the polymerization mechanism.

In copolymerization of pMMA-MM with *n*-BuA the molecular weight difference between both monomers caused a lower mobility of the MM, which appeared strongly at higher MM concentrations.

In FRP the relative reactivity of the MM decreased with increase in MM concentration, due to the diffusion control. In ATRP the diffusion control effect can be suppressed by extending the time scale of the polymerization. This leads at comparable monomer concentrations to much higher relative reactivity of the MM which is closer to the value of MMA since it is the low molecular weight model for the MM end-group. Due to the controlled nature of the ATRP reaction, the apparent molecular weights of the graft copolymer increased linearly with conversion and the polydispersities were lower than those obtained by FRP. However the polydispersity indices increased at high conversions, indicating side reactions such as termination or chain transfer.

The products of the pMMA-MM copolymerization with *n*-BuA using three different polymerization mechanisms such as FRP, ATRP and living anionic polymerization were analyzed by 2D chromatography[27] (HPLC (p*n*BuA elution under critical conditions (LACCC)[28])-GPC). The results are presented in Table 5. It has been found that the polymerization mixture composition depends strongly on the mechanism. Four main compounds could be identified: i) the poly(*n*BuA-*graft*-MMA) graft copolymer, which is the desired product; ii) poly(*n*BuA-*star*-MMA) that has only one pMMA graft incorporated in the p*n*BuA chain; iii) the remaining pMMA-MM and iv) p*n*BuA-homopolymer. In contrast to FRP that led to 63% graft copolymer, 17% star copolymer and 9% p*n*BuA homopolyer, the ATRP gave > 90% of the desired graft copolymer and less than 1% p*n*BuA homopolymer (Table 5). Using living anionic polymerization

techniques the lowest polydispersity value of the graft copolymer was obtained (M_w/M_n = 1.3 < 1.7 (FRP) < 1.8 (ATRP)). However there was 31% MM left and the distribution of the grafts in the graft copolymer is probably not random but strongly tapered, due to the reactivity differences of the comonomers that occurs strongly in anionic polymerization.

Table 5: Composition of polymerization mixture determined by 2D chromatography.

Mechanism	Percentage of compound after polymerization ($M_{n,app}$; M_w/M_n)			
	Graft copolymer p(*n*BuA-*g*-MMA)	Star copolymer p(*n*BuA-*star*-MMA)	Macromonomer pMMA-MM	Homopolymer p*n*BuA
FRP [a]	63 (54800; 1.7)	17	8*	9
ATRP [b]	91 (72600; 1.8)	6	1 (5900; 2.1)*	1
anionic [c]	40 (86000; 1.3)	18	31 (7800; 1.8)**	5

[a] AIBN; 60 °C; butyl acetate as solvent [3].
[b] methyl • -bromopropionate, Cu[dNbpy]$_2$Br, Cu^0; 90 °C; diphenyl ether as solvent[26].
[c] ethyl • -lithioisobutyrate, 2:1 complex of triisobuthylaluminium and CsF; -78 °C; toluene as solvent[29,30].
* methacryloyl head group.
** acryloyl head group.

1.5 Poly(*n*-butyl acrylate-*graft*-ethylene)[31]

Methacryloyloxy end-functionalized polyethylene macromonomer (pE-MM) with molecular weight of $M_n \sim 10000$ and polydispersity of $M_w/M_n < 1.04$ were prepared using a Pd catalyst[32-34]. Since the polyethylene was highly branched (106-92 branches per 1000 C) and amorphous the macromonomer was soluble in common solvents such as hexanes, THF, chloroform and also in *n*-butyl acrylate. Using ATRP techniques the MM could be copolymerized with *n*-butyl acrylate. The inverse reactivity ratio, determined by Jaacks method, was found to be highly dependent on the initial concentration of MM (Table 6). At low concentration and consequently decreased viscosity of the reaction mixture, the MM was consumed faster than the comonomer, owing to the higher reactivity of the methacryloyloxy group. This was manifested by $1/r_{nBuA} = 2.38$. At higher pE-MM concentrations (Table 6, entry 2-3), the viscosity of the solution increased lowering the mobility of the macromonomer and causing a decrease in the apparent reactivity. Nevertheless the polymerization was in all cases controlled which was demonstrated by the low polydispersity values (Table 6).

Table 6: Poly(n-butyl acrylate-g-ethylene) by ATRP of polyethylene macromonomer with n-butyl acrylate.

	$(Comp.)_0$[a] (wt%)	M_n ($\times 10^{-3}$)	M_w/M_n	Comp.[b] (wt%)	$1/r_{nBuA}$[c]
1	25.0	115	1.6	34.7	2.38
2	50.0	86	1.4	59.2	1.72
3	71.4	70	1.4	70.2	0.94

[a] Initial pE-MM weight % in monomers.

[b] Polyethylene weight % in the graft copolymer determined by the conversion of *n*-BuA and pE-MM.

[c] Reactivity ratios determined by Jaacks method.

Polymerization conditions:

1) *n*-BuA : pE-MM : DMDBHD (dimethyl 2,6-dibromoheptanedioate) : CuBr : PMDETA (N,N,N',N",N"-pentamethyldiethylenetriamine) = 1669:6.0:1:20:20, $[n\text{BuA}]_0 = 4.92$ mol/L; t = 15 h.
2) *n*-BuA : pE-MM : DMDBHD : CuBr : PMDETA = 546:6.3:1:10:10, $[n\text{BuA}]_0 = 3.48$ mol/L; t = 6.7 h.
3) *n*-BuA : pE-MM : DMDBHD : CuBr : PMDETA = 234:7.0:1:10:10, $[n\text{BuA}]_0 = 2.11$ mol/L; t = 15 h.

2 Graft copolymers by the "grafting from" approach

The "grafting from" approach uses a macroinitiator (MI) that carries initiation groups to start a polymerization reaction of a monomer. The synthesis of the MI allows the control of the main chain parameters (DP, M_w/M_n) as well as the pre-determination of side chain density and side chain distribution. The main difficulty in this approach is to ensure a uniform propagation of the side chains and furthermore to suppress chain coupling reactions.

The method is not restricted to linear MI, particles[35,36] and surfaces[37,38] were also successfully functionalized with initiating groups and used as MI to get access to e.g. inorganic organic hybrid materials.

2.1 Macroinitiators leading to graft copolymers with low graft density

Table 7: Graft copolymers from polyolefin macroinitiators.

	Macroinitiator			Monomer	Graft copolymer			
	Polymer	M_n ($\times 10^{-3}$)	M_w/M_n		Monomer (wt.-%)	M_n ($\times 10^{-3}$)	M_w/M_n	T_g (°C)
1	PIB[1)]	200	2.1	Sty[2)]	65	435	2.4	-64/93
		"	"	Sty	18	180	2.5	-57/ -
		"	"	MMA[3)]	68	300	3.5	-70/100
		"	"	MMA	15	200	3.5	-59/110
		108	2.3	IBuA[4)]	21	181	2.5	-10
2	PEGM[5)]	-	-	Sty	69	-	-	-15/108
				MMA	80	-	-	- /125
3	CSPE[6)]	14.9	2.3	Sty	-	85.6	1.8	-10/87
				MMA	-	26.3	1.8	-2
4	PVC[7)]	47.4	2.7	Sty	80	99.5	3.7	80
				MA	50	57.7	2.4	21
				MMA	60	83.6	4.9	111
				n-BuA[8)]	65	81.4	2.4	-19

[1)]PIB = poly(isobutylene-co-p-methylstyrene-co-p-bromomethylstyrene), [2)]Sty = styrene, [3)]MMA = methyl methacrylate, [4)]IBuA = isobornyl acrylate, [5)]PEGM = poly(ethylene-co-glycidyl methacrylate), [6)]CSPE = chlorosulfonated polyethylene, [7)]PVC = poly(vinyl chloride-co-vinyl chloroacetate), [8)]BuA = *n*-butyl acrylate.

2.1.1 Graft copolymers of poly(isobutene) [39-41]

Thermoplastic elastomers were prepared starting from commercially available partially brominated poly(isobutene-co-p-methystyrene) with 1.2 mole-% benzylic bromine (Exxpro™ elastomer), which was used as a macroinitiator to initiate ATRP of styrene[39-41], methyl methacrylate[41] and isobornyl acrylate[39] (Table 7, entry 1). The molecular weights of the graft copolymers increased linearly with conversion. Above a certain ratio of comonomer in the graft copolymer the glass transition temperatures of both backbone and grafts could be observed in DSC analysis, indicating microphase separation (Table 7). Combining soft (low T_g) polymers with hard glassy polymers lead to thermoplastic elastomers or impact strength modified plastics, if microphase separation takes place.

2.1.2 Graft copolymers from polyethylene[42]

Free radical polymerization methods were mainly used for the synthesis of graft copolymers from non-polar olefin backbones. "Grafting from" via irradiation initiation was mostly employed[43]. More recently, metallocene[44] and nitroxide-mediated[33] methods have been used to grow styrene grafts from ethylene and propylene backbones respectively.

Commercially available poly(ethylene-co-glycidyl methacrylate) was converted into a suitable ATRP macroinitiator by reaction of the epoxide groups with chloroacetic acid or 2-bromoisobutyric acid. From this pendant functionalized macroinitiator styrene and methyl methacrylate was grafted using ATRP conditions (Table 7, entry 2). The amount of incorporated comonomer could be controlled by the monomer conversion. The linear increase of the molecular weight with conversion and low polydispersities of $M_w/M_n < 1.4$ of the cleaved side chains indicated a controlled growing reaction. DSC analysis of purified samples showed two glass transitions, which were characteristic for polyethylene and polystyrene or poly(methyl methacrylate) segments respectively (Table 7).

2.1.3 Graft copolymers of chlorosulfonated polyethylene

Chlorosulfonated polyethylene (CSPE) is an elastomer that contains chlorine atoms and sulfonyl chloride groups randomly distributed on a polyethylene chain. Sulfonyl chloride groups are known to be good initiators for ATRP[45]. Therefore, CSPE can be used as macroinitiator in ATRP to produce graft copolymers[46,47]. Table 7 (entry 3) shows the results of CSPE grafting with styrene and MMA by ATRP.

2.1.4 Graft copolymers of poly(vinyl chloride)[48]

Graft copolymers of poly(vinyl chloride) with styrene and (meth)acrylates have been prepared by ATRP using a statistical copolymer of vinyl chloride with 1 mole-% vinyl chloroacetate as macroinitiator (Table 7, entry 4). For *n*-butyl acrylate polymerization the molecular weight of the graft copolymer increased with increasing incorporation of the monomer, while the glass transition temperature decreased. All graft copolymers prepared displayed only one glass transition temperature, indicating no sufficient microphase separation (Table 7).

2.1.5 Graft copolymers of polysiloxanes[49]

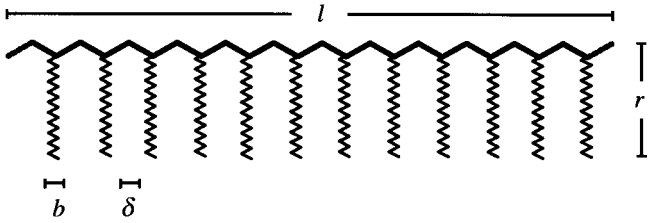
Graft copolymers composed in part of polysiloxanes can be prepared by using a hydrosilation reaction to introduce 2-(4-chloromethylphenyl)ethyldimethylsilane to the vinyl groups of poly(dimethyl-co-vinylmethylsiloxane). The obtained macroinitiator with pendant benzyl chloride functionalities can initiate the polymerization reaction of styrene under ATRP conditions. The resulting graft copolymer is an inorganic/organic composite material, consisted out of an inorganic backbone and organic grafts.

2.2 Macroinitiators leading to graft copolymers with high graft density[50-52]

The "grafting from" method is also a convenient route to polymer systems with high graft density. Well-defined, macroinitiators can be prepared that have ATRP initiation groups as side groups in each repeat unit. These can be accessed by transformation of a well-defined MI precursor (poly(2-trimethylsilyloxyethyl methacrylate; pHEMA-TMS) which has already been prepared by ATRP with 2-bromopropionyl bromide into poly(2-(2-bromopropionyloxy)ethyl methacrylate) (pBPEM)[50,52].

Molecular brushes can be prepared with homopolymer side chains of polystyrene and various polyacrylates with good control as indicated by the low over all polydispersity of the molecular brushes and the low polydispersities of the cleaved side chains $M_w/M_n = 1.2$ [52,53]. The resulting graft copolymers provide sufficient steric repulsion between the side chains to force the backbone into an extended worm-like conformation. The molecules are large enough to be resolved individually on mica surface using atomic force microscopy (AFM) in tapping mode.

A variety of different molecular parameters can be controlled using this method (Scheme 4): i) aspect ratio (l - axial length versus r - molecule radius); ii) side chain bulkiness (b - methyl < n-buthyl < t-buthyl acrylate side chains); iii) main chain architecture (block copolymer); iv) graft density (• - spacing in between the grafts); v) graft density gradient (• •); vi) side chain architecture (block copolymer side chains). Thus, ATRP has provided the means to prepare densely grafted macromolecules with more well-defined dimensions without the subsequent fractionation at size exclusion columns necessary.



Scheme 4: Molecular parameters in a molecular brush.

Densely grafted polymer systems are also accessible by "grafting through" techniques in combination with ATRP[54]. However, the homopolymerization of macromonomers presents a limitation as far as high targeted DP is concerned.

Conclusions

Atom transfer radical polymerization (ATRP) was used to synthesize a variety of graft copolymers, differing in main and side chain polymer types. Using "grafting through" and "grafting from" methods, the molecular parameters such as the degree of polymerization of and the polydispersity of main and side chain polymer, graft density and graft distribution could be controlled.

Acknowledgment

Beers, K. L.; Gaynor, S. G.; Hong, S. C.; Kickelbick, G.; Kowalewski, T.; Miller, P. J.; Nakagawa, Y.; Pyun, J.; Peterson, M. L.; Paik, H.-j.; Patten, T. E.; Roos, S. G; Shinoda, H.; Teodorescu, M.; Wang, J. S.

This work was financially supported by the National Science Foundation, ATRP/CRP Consortia at CMU and Deutsche Forschungsgemeinschaft (DFG, Germany).

(1) Rempp, P. F.; Lutz, P. J. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, **1989**; Vol. 6; p. 403.
(2) Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Adv. Polym. Sci.* **1998**, *135*, 1.
(3) Roos, S. G.; Müller, A. H. E.; Kaufmann, M.; Siol, W.; Auschra, C. *ACS Symp. Ser.* **1998**, *696*, 209.
(4) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(5) Matyjaszewski, K. *Controlled Radical Polymerizations*; American Chemical Society: Washington,

DC, **1998**; Vol. 685.
(6) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(7) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(8) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(9) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.
(10) Matyjaszewski, K.; Wei, M.; Xia, J.; McDermott, N. E. *Macromolecules* **1997**, *30*, 8161.
(11) Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 8576.
(12) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamotao, M. *Macromolecules* **1997**, *30*, 2249.
(13) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, K. L.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
(14) Hawker, C. J.; Malmstrom, E. E.; Frechet, J. M. J.; Leduc, M. R.; Grubbs, R. B.; Barclay, G. G. *Controlled Radical Polymerization*; American Chemical Society: Washington, D.C., **1998**; Vol. 685.
(15) Patten, T. E.; Matyjaszewski, K. *Adv. Mat.* **1998**, *10*, 901.
(16) Schulz, G. O.; Milkovich, R. *J. Appl. Polym. Sci.* **1982**, *27*, 4773.
(17) Mishra, M. K. *Macromolecular Design: Concept and Practice - Macromonomers, etc.*; Polymer Frontier International: New York, **1994**.
(18) Meijs, G. F.; Rizzardo, E. *J. Macromol. Sci., Rev. Macromol. Chem.* **1990**, *C30*, 305.
(19) Radke, W.; Müller, A. H. E. *Macromol. Chem., Macromol. Symp.* **1992**, *54*, 583.
(20) Shinoda, H.; Matyjaszewski, K. *Macromolecules* **2001**, *submitted.*
(21) Shinoda, H.; Miller, P. J.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 3186.
(22) Matyjaszewski, K.; Beers, K. L.; Kern, A.; Gaynor, S. G. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 823.
(23) Schunk, T. C.; Long, T. E. *J. Chromatogr.* **1995**, *A692*, 221.
(24) Jaacks, V. *Macromol. Chem.* **1972**, *161*, 161.
(25) Roos, S. G.; Müller, A. H. E.; Matyjaszewski, K. *ACS Symp. Ser.* **2000**, *768*, 361.
(26) Roos, S. G.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 8331.
(27) Müller, A. H. E.; Roos, S. G.; Schmitt, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40*, 140.
(28) Pasch, H.; Much, H.; Schulz, G.; Gorshkov, A. V. *LC GC Int.* **1992**, *5*, 38.
(29) Schlaad, H.; Schmitt, B.; Müller, A. H. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1389.
(30) Schmitt, B. Dissertation, University of Mainz, 1999.
(31) Hong, S. C.; Matyjaszewski, K.; Gottfried, A. E.; Brookhart, M. *Polymeric Materials: Science and Engineering* **2001**, *84*, *in press.*
(32) Fox, P. A.; Waymouth, R. M.; Hawker, C. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40*, 872.
(33) Stehling, U. M.; Malmstrom, E. E.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* **1998**, *31*, 4396.
(34) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.
(35) Von Werne, T.; Patten, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 7409.
(36) Pyun, J.; Matyjaszewski, K.; Kowalewski, T.; Savin, D.; Patterson, G.; Kickelbick, G.; Huesing, N. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, *42*, 223.
(37) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716.
(38) Husseman, M.; Malmstroem, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424.
(39) Gaynor, S. G.; Matyjaszewski, K. *Controlled Radical Polymerizations*; American Chemical Society: Washington, DC, 1998; Vol. 685, p. 396.
(40) Fonagy, T.; Ivan, B.; Szesztay, M. *Macromol. Rapid Commun.* **1998**, *19*, 479.
(41) Hong, S. C.; Pakula, T.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2001** *submitted.*
(42) Matyjaszewski, K.; Teodorescu, M.; Miller, P.; Peterson, M. L. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2440.
(43) Simonazzi, T.; De Nicola, A.; Aglietto, M.; Ruggieri, G. *In Comprehensive Polymer Science, 1st Suppl.;* Pergamon Press: Oxford, **1992**, p. 133.
(44) Chung, T. C. *ACS Symp. Ser.* **2000**, *749*, 104.
(45) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.
(46) Matyjaszewski, K.; Beers, K. L.; Coca, S.; Gaynor, S. G.; Miller, P. J.; Paik, H.-j.; Teodorescu, M.

Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **1999**, *40*, 95.
(47) Matyjaszewski, K.; Gaynor, S. G.; Coca, S. *PCT Int. Appl.* **1998**.
(48) Paik, H.-j.; Gaynor, S. G.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1998**, *19*, 47.
(49) Nakagawa, Y.; Miller, P. J.; Matyjaszewski, K. *Polymer* **1998**, *39*, 5163.
(50) Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Möller, M. *Macromolecules* **1998**, *31*, 9413.
(51) Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Prokhorova, S. A.; Möller, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40*, 446.
(52) Börner, H. G.; Beers, K. L.; Matyjaszewski, K.; Sheiko, S. S.; Möller, M. *Macromolecules* **2001**, *in press.*
(53) Beers, K. L.; Matyjaszewski, K. *unpublished results.*
(54) Yamada, K.; Miyazaki, M.; Ohno, K.; Fukuda, T.; Minoda, M. *Macromolecules* **1999**, *32*, 290.