Novel Segmented Copolymers by Combination of Controlled Ionic and Radical Polymerizations

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Summary. Transformation of different living and non-living polymerization mechanisms to controlled/"living" atom transfer radical polymerization (ATRP) in order to prepare block and graft copolymers is described. The synthesis and characterization of macroinitiators and the resulting segmented copolymers is discussed.

Introduction

Block and graft copolymers represent valuable polymeric materials, as their properties can be designed by a proper choice of the monomers that form the polymeric segments. For example, impact resistant materials or thermoplastic elastomers can be obtained when the constituent blocks of the segmented copolymers are thermodynamically incompatible and microphase separation occurs. Also, amphiphilic copolymers with such applications as hydrogels, stabilizers, surface-modifying agents, compatibilizers in polymer blends, etc. have been prepared[1,2].

Depending on the monomers involved, the segmented copolymers can be synthesized by employing the same polymerization mechanism for all blocks, or by using a combination of different mechanisms. In the former case the synthesis is accomplished by the appropriate sequential addition of the monomers if block copolymers are targeted. In the latter case, the most often used procedure involves the conversion of the functional end groups of the first block (in the case of block copolymers) or the groups distributed along the chain (in the case of graft copolymers) to initiating sites for the polymerization of the second monomer. This approach is employed when the monomers involved do not polymerize by the same mechanism, examples include conversion of vinyl polymerization to ring opening polymerization, cationic to anionic, condensation to radical polymerization, etc.[3,4]

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The controlled/"living" polymerizations allow for the preparation of well-defined polymers, i. e. polymers with predetermined molecular weights and low polydispersities, and they have been extensively used for the preparation of segmented copolymers. Until lately, well-defined segmented copolymers could be obtained only by ionic polymerizations. Due to the lack of control of molecular weight and polydispersity, the free-radical methods led to ill-defined polymers, very often accompanied by a certain amount of homopolymer and/or crosslinked material[3,4]. However, recently free-radical techniques have also became available for the preparation of well-defined polymers. The most important types of controlled radical polymerizations (CRP) are: i) stable free-radical polymerization (SFRP), which employs nitroxyl radicals[5]; ii) atom transfer radical polymerization (ATRP), which uses complexes of transition metals in conjunction with alkyl halides[5]; iii) reversible addition-fragmentation chain transfer polymerization (RAFT), which uses dithioesters together with a free-radical initiator[6] or other degenerative transfer processes[7]. So far only SFRP and ATRP have been used to prepare segmented copolymers by combination with other polymerization mechanisms. Table 1 (block copolymers) and Table 2 (graft copolymers) summarize the results published on this subject.

In all the cases presented in Table 1, the block copolymer synthesis consists in at least 2 steps: the macroinitiator synthesis and the polymerization of the second monomer. A particular case is represented by the "one pot" synthesis, when a double-headed initiator is used to simultaneously initiate the formation of both blocks, by two different mechanisms. The method has been used to prepare a polyoxazoline - PSt block copolymer by simultaneous cationic ROP and SFRP[39], and PCL-PSt block copolymers by simultaneous anionic ROP and SFRP or ATRP[40].

In our continuing effort to develop new materials by ATRP, we addressed the field of block and graft copolymers by transformation reactions. The present paper aims to present our work concerning the preparation of segmented copolymers by using controlled/"living" atom transfer radical polymerization in conjunction with another polymerization mechanism, such as anionic, cationic, ROMP, conventional radical or step-growth polymerization. Detailed results are shown in Table 3 (block copolymers) and Table 4 (graft copolymers).

Table 1. Examples of block copolymers prepared by CRP using transformation reactions

Entry	Macroinitiator		Second block		Ref.
	Polymer	Polymn. mechanism	Monomer	Polymn. mechanism	
1	PSt, PBut	anionic	acrylates, St	SFRP	8,9)
2	PEO, PCL, PDMS	anionic ROP	St	SFRP	10-14)
3	PTHF, PCHO	cationic ROP	St	SFRP	15-17)
4	polycarbonate	condensation	St	SFRP	18)
5	PBA, PMMA, PIP	conv. radical	St	SFRP	19)
6	PSt	SFRP	CL	anionic ROP	12)
7	PSt	SFRP	phos + bph, aryleneX$_2$	condensation	18,20)
8	PSt, PEB	anionic	St, 4-acetoxySt MA, BA, MMA	ATRP	21,22)
9	PEO, PCL	anionic ROP	St, MMA, t-BA	ATRP	23-26)
10	PSt, PIb	cationic	St, 4-acetoxySt MA,MMA, IBA	ATRP	27-30)
11	PTHF, PDMS	cationic ROP	St,MA,MMA	ATRP	31,32)
12	PNB, PDCPD	ROMP	St, MA	ATRP	33)
13	PBA, PVDF, PSt, PVAc	conv. radical	St, BA	ATRP	34-36)
14	PMPSil, polyarylene, PSulfone	condensation	St, BA	ATRP	20,37,38)
15	PMMA	ATRP	CL	anionic ROP	12)

PBut - polybutadiene; PSt - polystyrene; PEO - poly(ethylene oxide); PCL - poly(e-caprolactone); PTHF - polytetrahydrofuran; PCHO - poly(cyclohexane oxide); phos - phosgene; bph - bisphenol A; PEB - poly(ethylene-*co*-butylene); PIb - polyisobutylene; PDMS - polydimethylsiloxane; PNB - polynorbornene; PDCPD - polydicyclopentadiene; PVAc - poly(vinyl acetate); PBA - poly(butyl acrylate); PVDF - poly(vinylidene fluoride); PMPSil - poly(methylphenylsilane); PSulfone - polysulfone; PMMA - poly(methyl methacrylate); aryleneX$_2$ - arylene dihalogen; MA - methyl acrylate; IBA - isobornyl acrylate

Table 2. Examples of graft copolymers prepared by CRP using transformation reactions

Entry	Macroinitiator		Second block		Ref.
	Polymer	Polymn. mechanism	Monomer	Polymn. mechanism	
1	PSt	conv. radical	St	SFRP	41)
2	PCL	anionic ROP	MMA	ATRP	42)
3	PIb	cationic	St, IBA	ATRP	43,44)
4	polysiloxane	cationic ROP	St	ATRP	32)
5	PEPDM	coordinative	MMA	ATRP	45)
6	CSPE, PE, PVC	conv. radical	St, MA, BA, MMA	ATRP	46-48)
7	PMPSil	cond.	St	ATRP	49)

PEDM - ethylene-propylene-diene terpolymer; CSPE - chlorosulfonated polyethylene; PE - polyethylene; PVC - poly(vinyl chloride).

Results and discussion

Almost all polymerization mechanisms were combined with ATRP in order to prepare block copolymers. Whenever possible, the first block was prepared in a living manner (Table 3, entries 1-12, 14-17), which allowed a better control of the molecular weights, polydispersities and end functionalities. Thus, "living" anionic polymerization of styrene was terminated with styrene oxide/2-bromoisobutyryl bromide, and after isolation, the polymer was used to initiate ATRP of (meth)acrylates (Table 3, entries 1-3). "Living" cationic polymerizations of styrene and isobutene were also used to prepare ATRP macroinitiators (Table 3, entries 4-9). In the latter case a difunctional polyisobutene terminated with several units of styrene was employed in order to prepare ABA-type block copolymers. In both cases no transformation chemistry was needed because the ATRP initiating sites naturally resulted due to the polymerization characteristics. Mono- (Table 3, entries 10, 11) and difunctional (Table 3, entry 12) PTHF macroinitiators were synthesized by initiating THF polymerization with 2-bromopropionyl bromide/silver triflate or by deactivating a difunctional "living" PTHF with sodium 2-bromopropionate, respectively.

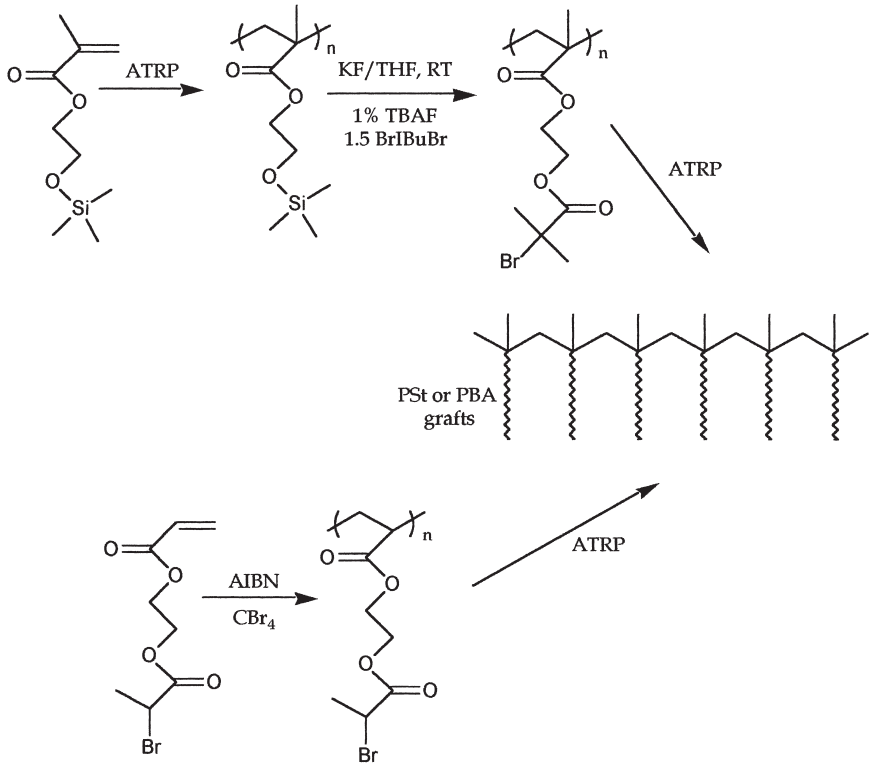
ROMP was also successfully employed to prepare block copolymers in conjunction with ATRP (Table 3, entries 14-17). Polynorbornene and polydicyclopentadiene were

synthesized in a "living" manner by using the Schrock catalyst, followed by deactivation with p-(bromomethyl)benzaldehyde to provide a bromobenzyl terminated macroinitiator.

Poly(dimethylsiloxane), commercially available with Si-H end groups and a polysulfone with hydroxy end groups, prepared by the condensation polymerization of bisphenol A and 4,4'-difluorosulfone, were converted to ATRP macroinitiators by reacting the terminal groups with vinylbenzyl chloride in the presence of a Karstedt catalyst or with 2-bromopropionyl bromide, respectively (Table 3, entries13, 19).

Conventional radical polymerization was combined with ATRP in both ways in order to prepare block copolymers. When the first block was prepared by conventional radical polymerization, the macroinitiator resulted directly by using either a thermal initiator containing the ATRP initiating group (Table 3, entry 19) or CCl_4 as a telogen (Table 3, entry 18). The other way involves the preparation of the first block by ATRP initiated by an initiator containing an thermolabile azo group, which can be decomposed later, at a higher temperature, to initiate the polymerization of a second monomer by conventional radical polymerization (Table 3, entry 22). Because of the lack of control in the conventional radical polymerization step, the synthesized block copolymers had higher polydispersities.

Commercially available polymers were used as macroinitiators or precursors in almost all graft copolymer syntheses. Thus, brominated poly(isobutene-co-p-methylstyrene) with 1.2 mole-% bromobenzyl groups (PIb-Br), chlorosulfonated polyethylene with sulfonyl chloride groups as ATRP initiating sites and a statistical copolymer of vinyl chloride with 1 mole-% vinyl chloroacetate (PVCA) have been used as macroinitiators without any further transformation (Table 4). In other cases, transformation reactions were carried out in order to convert the functional groups of the precursor into initiating sites for ATRP. Thus, the vinyl groups of poly(dimethyl-co-vinylmethylsiloxane) (PSilox) were reacted with 2-(4-chloromethylphenyl)ethyldimethylsilane to produce a polymer with pendant benzyl chloride functionalities, which was used to initiate ATRP of styrene (Table 4, entry 3). Similarly, commercially available poly(ethylene-co-glycidyl methacrylate) (PEGM) was converted to a macroinitiator by reacting the epoxy groups with chloroacetic acid in the presence of tetrabutylammonium hydroxide in xylene at 115°C (Table 4, entry 6).



Scheme 1

Acknowledgment

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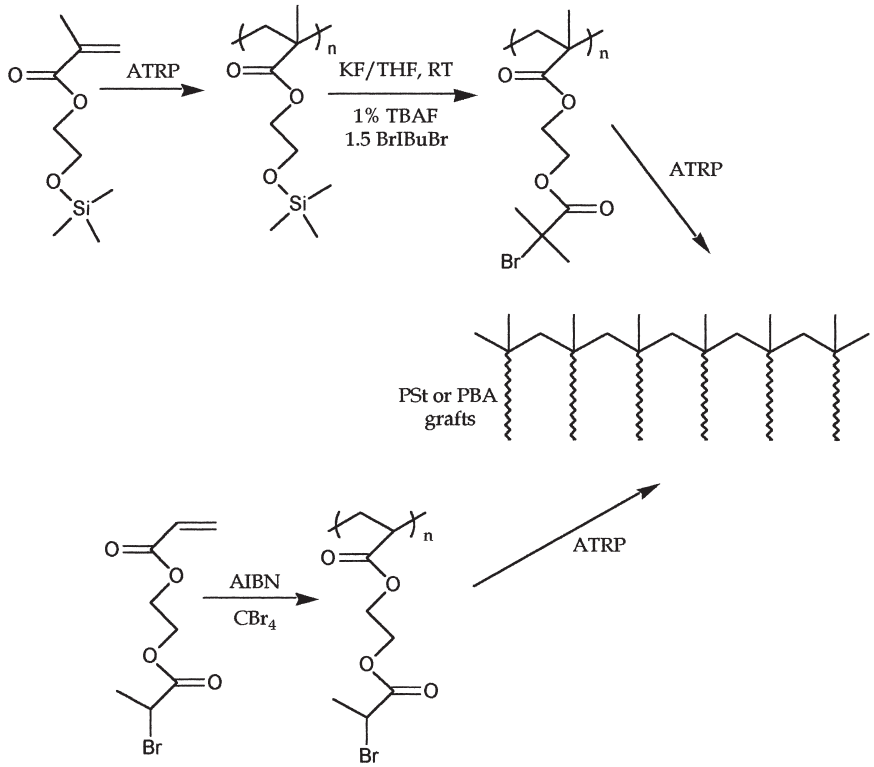
Table 4. Graft copolymers by combining different polymerization mechanisms with ATRP

No	Macroinitiator					Mon.	Graft copolymer				Ref
	Polym	Polymn mech.	M_n (10^{-3})	M_w/M_n	T_g /°C		Mon. /wt-%	M_n (10^{-3})	M_w/M_n	T_g /°C	
1	PIb-Br	cationic	108	2.3	-60	St	69	250	2.4	-60/98	43)
2	"	"	"	"	"	IBA	21	181	2.5	-10	"
3	PSilox	CROP	6.6	1.8	-	St	54	14.8	2.1	-	32)
4	CSPE	radical	14.9	2.32	-15	St	-	85.6	1.78	-10/87	46)
5	"	"	"	"	"	MMA	-	26.3	1.75	-2	"
6	PEGM	"	-	-	-15	St	69	-	-	-15/108	48)
7	PVCA	"	47.4	2.66	83	St	80	99.5	3.72	80	47)
8	"	"	"	"	"	MA	50	57.7	2.40	21	"
9	"	"	"	"	"	MMA	60	83.6	4.94	111	"
10	"	"	"	"	"	BA	65	81.4	2.44	-19	"
11	PBPEA	"	27.3	2.3	-	BA	-	1,500	1.5	-	-

A particular case of graft copolymers is represented by densely grafted or "brush" copolymers. They were synthesized using macroinitiators with ATRP initiating sites at each repeating unit along the backbone, prepared either by free radical polymerization of 2-(2-bromopropionoxy)ethyl acrylate (BPEA) (Table 4, entry 11) or by esterification with 2-bromoisobutyryl bromide of well-defined poly(2-trimethylsilyloxyethyl methacrylate), which has already been prepared by ATRP (Scheme 1)[50].

Conclusions

Atom transfer radical polymerization (ATRP) has been successfully used in combination with other living and non-living polymerization mechanisms to prepare block and graft copolymers.



Scheme 1

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