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Transformation of "Living" Carbocationic and other Polymerizations to Controlled/"Living" Radical Polymerization

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Abstract: Transformation of "living" carbocationic polymerization of styrene and isobutene to controlled atom transfer radical polymerization (ATRP) is described and formation of the corresponding AB and ABA block copolymers with styrene (St), methyl methacrylate (MMA, methyl acrylate (MA) and isobornyl acrylate (IBA) was demonstrated. A similar approach was applied to the cationic ring opening polymerization of tetrahydrofuran leading to the AB and ABA block copolymers with St, MMA and MA using ATRP. Site transformation approach was also used for the ring opening metathesis polymerization of norbornene and polycondensation systems using polysulfone as an example. In both cases, AB and ABA block copolymers were efficiently formed with styrene and acrylates.

INTRODUCTION

Controlled/"living" polymerization methods offer the best way to prepare well-defined polymers (controlled molecular weight, polydispersities, and terminal functionalities). In these systems the contribution of chain breaking reactions is small, the polymerization proceeds until all of the monomer has been consumed and further additions of monomer result in continued polymerization (Ref. 1, 2). Controlled/"living" polymerization can proceed by anionic (Ref. 3, 4), cationic (Ref. 5 - 7), group transfer (Ref. 8), metathesis (Ref. 9 - 11), Ziegler- Natta (Ref. 12, 13) or radical mechanisms (Ref. 14 - 19).

The synthesis of block copolymers usually requires efficient controlled/"living" polymerization (Ref. 20). Controlled/"living" polymerization techniques give several powerful tools for synthesis of block and graft copolymers with well-defined structure: (a) sequential monomer addition, (b) coupling reaction of "living" chains, (c) reaction of end-functionalized polymer. The sequential monomer addition for block copolymers using two monomers can be carried out simply in one-pot, but the means of propagation for the second monomer should,

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accordingly, be the same, which sometimes limits the range of monomer combinations (Ref. 21). Another approach for block copolymers is the coupling reactions of two "living" homopolymers with opposite charges (e.g. carbocationic with group transfer polymerization) or by using coupling agents of two living chains of the same type (e.g. anionic or cationic). The reaction of end-functionalized polymer involves the transformation of chain ends after first monomer polymerization is complete into another type of initiating site with a completely different nature. Using this approach, Richards and co-workers developed methods to interconvert anionic and cationic or Ziegler-Natta processes (Ref. 22 - 24). Several papers report well-defined block copolymers by the transformation of initiating sites from "living" cationic to "living" anionic polymerization (Ref. 25 - 28). A common feature of these techniques is that they include many steps and the number of monomers is limited to those which can be polymerized by cationic or anionic methods.

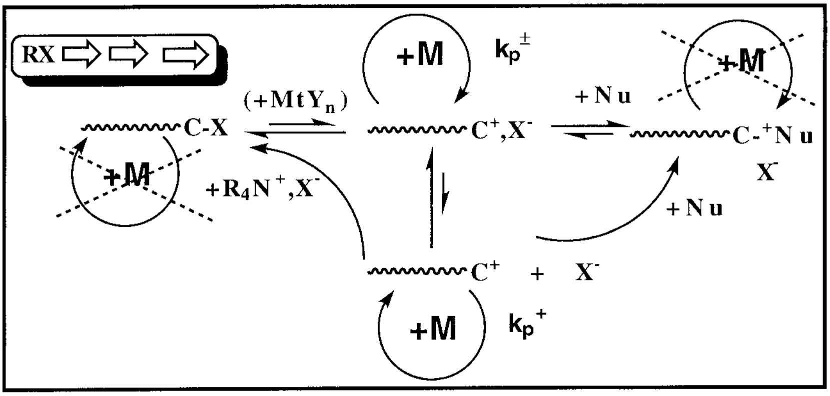
This article will focus on the transformation of controlled/"living" ionic polymerization, primarily cationic polymerization into controlled/"living"atom transfer radical polymerization (ATRP).

RESULTS AND DISCUSSION

Current status of "living" carbocationic polymerization

There are several approaches to control carbocationic polymerization. They include use of alkyl halides in combination with relatively weak Lewis acids to assure dynamic equilibration with growing carbocations, application of nucleophiles which scavenge growing carbocations and also addition of salts which convert rapidly free ions to the corresponding ion pairs. The dormant species dominate in all of these systems as shown in Scheme 1.

Scheme 1



Dormant species preserve their functionalities after deactivation of Lewis acids. For example, when alkyl halide/Lewis acids are used as initiators in polymerization of styrene, vinyl ethers and isobutene, polymers with terminal halogen atoms and with high degree of functionalities have been isolated. This feature is very important for the subsequent transformation process.

Controlled carbocationic polymerizations are multicomponent systems and it is useful to understand role of all components (Ref. 29).

1. Alkyl halides, RX, should ionize better than the corresponding dormant species, ...-C-X. Thus, it is useful to use groups R which stabilize carbocations such as those with alkoxy substituents or tertiary rather than secondary halides. In addition, a leaving group, X, in the initiator should be at least as nucleofugic as that in dormant species. Since the leaving groups at the chain end and those attached to Lewis acid exchange, it is useful to use either acetoxy or alkoxy derivatives, to accelerate the initiation process.
2. Lewis acid, MtY_n should ionize both the RX and ...-C-X species reversibly and dynamically. Neither too strong nor too weak Lewis acids are efficient. The strength of the Lewis acid may be affected by some additives.
3. The role of the nucleophiles, Nu, in the system seems to be most controversial. It has to be realized that nucleophiles may, and in many systems do, act in several different ways (Ref. 29).They can scavenge carbocations by reversible formation of onium ions. They can interact with and reduce strength of Lewis acids. In both ways they will accelerate exchange reactions by reducing lifetime of carbocations. Some nucleophiles may also trap protons.
4. Salts can also act in several different ways. They do suppress dissociation of carbocationic ion pairs by common ion effect (Ref. 30, 31).Sometimes they may also increase ionization by ionic strength effect and also by exchanging leaving groups in the special salt effect (Ref. 32, 33).In this way they may also modify structure of Lewis acids.
5. Solvents play an important role as in any ionic reactions. They affect dissociation constant of ion pairs and they may accelerate deactivation of carbocations. They may also affect ratios of propagation to chain breaking reactions.
6. Temperature has a very strong effect on carbocationic polymerization. Temperature should be always as low as possible to reduce the effect of transfer (Ref. 34).
7. Hindered pyridines primarily trap protons but, in some systems they may also act as nucleophiles and, after protonation, may act as salts (Ref. 35, 36).
8. Concentrations of monomer and initiator have to be carefully selected. High $[M]_0$ is useful to increase ratio of propagation to transfer to counterion. However, high $[M]_0$ increases propagation rate in comparison with the rate of exchange reactions and may lead to higher polydispersities.

High initiator concentration is useful to reduce contribution of transfer, but high $[I]_0$ results in shorter polymer chains which will have less exchange steps and may increase polydispersities.

Thus, the ratio $[M]_o/[I]_o$, which defines polymerization degree, has to be carefully chosen and should be limited to values at which chain breaking reactions are insignificant, e.g. in the case of monomer transfer:

$$DP \approx \Delta[M]/[I]_o \leq 0.1\ k_p/k_{trM}$$

At the same time, degrees of polymerization should be large enough to form polymers with sufficently low polydispersities. The polydispersites are defined by conversion, p, the ratio of propagation and deactivation rate constants (k_p/k_{deact}), concentration of the initiator and deactivator ($[D]_o$) :

$$M_w/M_n = 1 + (k_p/k_{deact})\ ([I]_o/[D]_o)\ (2/p - 1)$$

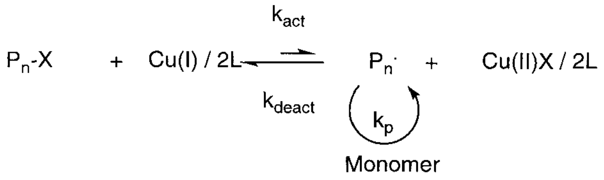
For the synthesis of block copolymers it is also very important to preserve activities of all chains until the second monomer is added. Thus, shelf-time is important, since a system can become totally inactive in spite of final low polydispersities, if it is kept for a too long time (Ref. 37).

Atom Transfer Radical Polymerization

In the last few years many efforts have been devoted to developments of controlled/"living" radical polymerization. Inifer or iniferter methodology (Ref. 14),stable free radicals such as TEMPO (Ref. 15, 38), various organometalic species (Ref. 39), degenerative transfer(Ref. 40) and atom transfer radical polymerization (ATRP)(Ref. 16 - 18, 41) were developed. ATRP seems to be the most robust of these systems.

The extension of atom transfer radical addition (ATRA)(Ref. 42, 43) to atom transfer radical polymerization (ATRP) provides a new and efficient way to conduct a controlled/"living" radical polymerization. With a variety of alkyl halides, R-X (X=Cl or Br), as the initiators and a transition metal species complexed by suitable ligand(s), CuX / 2,2'-bipyridine, as the catalyst, ATRP of vinyl monomers such as styrene, acrylates, methyl methacrylates, and acrylonitrile proceeds in a "living" fashion (Ref. 16 - 49). The resulting polymers have a degree of polymerization predetermined by $\Delta[M]/[I]_o$ up to $M_n \approx 10^5$ and low polydispersity, $1.1 < M_w/M_n < 1.5$. For example, when an alkyl chloride, 1-PhEtCl is used as initiator, and a CuCl/4,4'-diheptyl-2,2'-bipyridine or 4,4'-di-(5-nonyl)-2,2'-bipyridine complex is used as catalyst, styrene polymerizes by repetitive atom transfer radical additions to yield a well-defined, high molecular weight polymer, with narrow molecular weight distribution (M_w/M_n=1.05) (Ref. 50). Under appropriate conditions, the contribution of termination becomes insignificant and polymerization occurs according to Scheme 2.

Scheme 2



The rate of polymerization is first order with respect to monomer, alkyl halide, and the transition metal complexed by two bipyridine ligands. The reaction is negative first order with respect to the deactivator ($CuBr_2$/2bipy) and molecular weight scales reciprocally with $[\text{Initiator}]_0$ (Ref. 51).

ATRP is a versatile tool for preparation of random (Ref. 47), block (Ref. 52) alternating (Ref. 49) and gradient copolymers (Ref. 47, 53) with controlled molecular weights, narrow polydispersities and desired architectures. There are a multitude of initiators for ATRP. Any alkyl halide with activated substituents on α-carbon such as an aryl, carbonyl, or allyl can be used, in addition to polyhalogenated compound (CCl_4, $HCCl_3$) and those with weak X bonding such as N-X, S-X, O-X, etc.(Ref. 18, 52).This includes not only low molar mass compounds but macromolecular species as well, used to form the corresponding block/graft copolymers. Some pseudohalogens, thiocyanates for example, have also been used successfully for the polymerization of acrylates and styrenes (Ref. 54).

Block Copolymers by Transformation of "Living" Carbocationic into Controlled Atom Transfer Radical Polymerization

Recently, we reported a general method of transformation of "living" carbocationic into "living" radical polymerization, and successful preparation of block copolymers, without any modification of initiating sites (Ref. 55 - 57). For example, polystyrene with chlorine termini, synthesized by "living" cationic polymerization without any transformation, was used as an efficient macroinitiator for homogeneous "living" atom transfer radical polymerization of styrene and (meth)acrylates. By the same procedure, ABA-type block copolymers with PIB middle block obtained cationically and flanked by styrene or meth(acrylate) outer blocks were prepared (Ref. 57).

SYNTHESIS OF POLY(STYRENE-B-STYRENE), POLY(STYRENE-B-METHYL ACRYLATE) AND POLY(STYRENE-B-METHYL METHACRYLATE) COPOLYMERS (REF. 55)

Macroinitiators based on polystyrene with chlorine chain-ends were prepared by "living" cationic polymerization of styrene with 1-PhEtCl/SnCl4 initiating system in the presence of *n*-Bu$_4$NCl at -15°C in methylene chloride in a Schlenck flask under dry nitrogen. Subsequently, polystyrene with chlorine chain end, polystyrene-Cl, was used to initiate homogeneous ATRP of styrene, methyl acrylate, and methyl methacrylate in the presence of catalyst based on CuCl and 4,4'-di-(5-nonyl)-2,2'-bipyridine, dNbipy. Table 1 summarizes representative polymerization results in cationic polymerization of styrene (exp. 1), and homogeneous ATRP of styrene (St) (exp. 2), methyl acrylate (MA) (exp. 3) and methyl methacrylate (MMA) (exp. 4), initiated with polystyrene-Cl (PSt-Cl) and catalyzed by CuCl/dNbipy.

Table 1. Results obtained by transformation of "living" cationic to "living" radical polymerization

#	Monomer	Initiating system	Temp°C	$M_{n,th}$	$M_{n,exp}$	M_w/M_n
1	St	1-PhEtCl/SnCl$_4$/n Bu$_4$NCl	-15	2080	2100	1.17
2	St	PSt-Cl/CuCl/dNbipy	100	5100	5080	1.10
3	MA	PSt-Cl/CuCl/dNbipy	100	6200	6330	1.20
4	MMA	PSt-Cl/CuCl/dNbipy	100	10100	11090	1.57

Conditions: Exp. 1 $[St]_0$ =1 mol/L, $[1\text{-PhEtCl}]_0$ = 5x10^{-2} mol/L, $[1\text{PhEtCl}]_0/[SnCl_4]_0/[nBu_4NCl]_0$ = 1/5/2, CH_2Cl_2 solvent, conversion =98 %; Exp. 2 $[St]_0$ =3 mol/L, $[\text{PSt-Cl}]_0$ =0.1 mol/L, $[\text{PSt-Cl}]_0/[CuCl]_0/[dNbipy]_0$ = 1/1/2, $C_6H_5CH_3$ solvent, conversion =98.5 %; Exp.3 $[MA]_0$ =4.76 mol/L, $[\text{PSt-Cl}]_0$ =0.1 mol/L, $[\text{PSt-Cl}]_0/[CuCl]_0/[dNbipy]_0$ = 1/1/2, $C_6H_5CH_3$ solvent, conversion =99.5 %; Exp.4 $[MMA]_0$ =8 mol/L, $[\text{PSt-Cl}]_0$ =0.1 mol/L, $[\text{PSt-Cl}]_0/[CuCl]_0/[dNbipy]_0$ = 1/1/2, $C_6H_5CH_3$ solvent, conversion =97.5 %

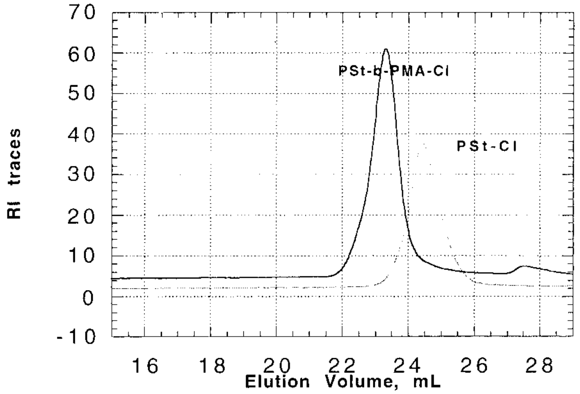


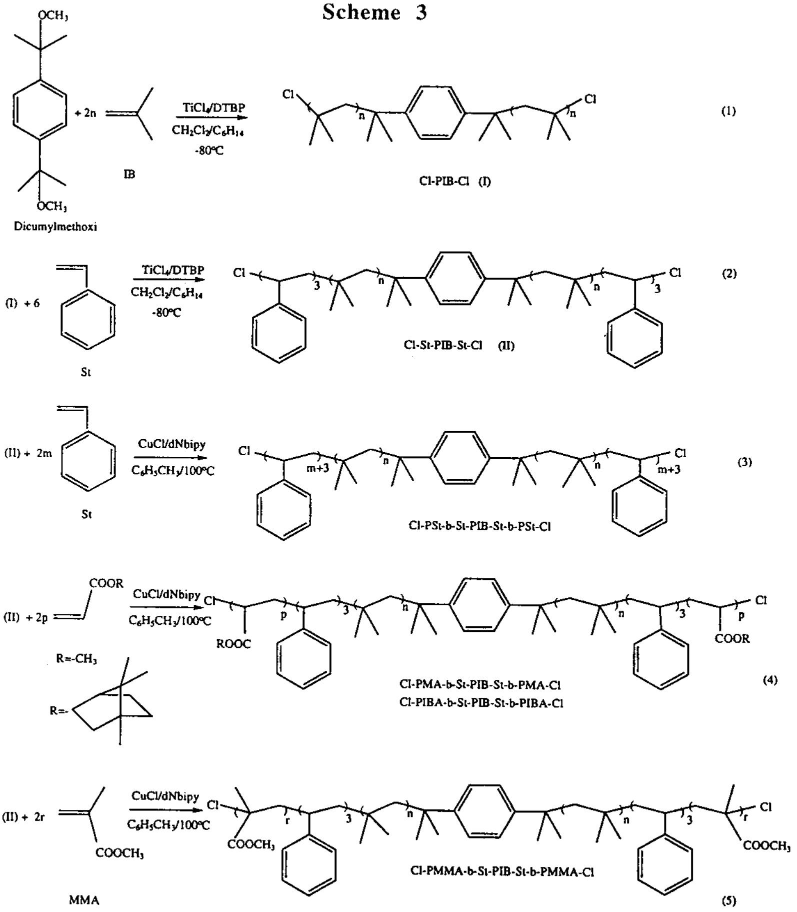
Fig. 1. The GPC chromatograms for PSt-Cl and PSt-b-PMA-Cl polymers shown in Table 1 (exp.1 and 3)

The GPC chromatogram of starting PSt-Cl and PSt-b-PMA-Cl copolymer is illustrated in Figure 1. The reaction mixtures from block copolymer synthesis were diluted with THF and injected directly into GPC in order to avoid any fractionation of the polymer sample during isolation. The GPC measurements showed that molecular weight distribution of block copolymer is unimodal and narrow. No signal attributed to starting macroinitiators is detected.

ABA-TYPE BLOCK COPOLYMERS COMPRISING RUBBERY POLYISOBUTENE MIDDLE SEGMENT (REF. 56)

α,ω-Difunctional PIB, Cl-PIB-Cl capped with a few (i.e., ≈ 3)units of styrene, Cl-St-PIB-St-Cl, synthesized by "living" carbocationic polymerization, without any transformation, was an efficient difunctional initiator in "living" ATRP of styrene (St), methyl

Scheme 3



acrylate (MA), isobornyl acrylate (IBA) and methyl methacrylate (MMA) leading to Cl-PSt-b-St-PIB-St-b-PSt-Cl, Cl-PMA-b-St-PIB-St-b-PMA-Cl, Cl-PIBA-b-St-PIB-St-b-PIBA-Cl, and Cl-PMMA-b-St-PIB-St-b-PMMA-Cl triblock copolymers, as shown in Scheme 3.

Table 2 summarizes representative polymerization results in cationic polymerization of isobutene and styrene (exp. 1 and 6), and homogeneous ATRP of St (exp. 2 and 7), MA (exp. 3 and 8), MMA (exp. 4 and 9) and IBA (exp. 5), initiated with Cl-St-b-PIB-St-Cl and catalyzed by CuCl/dNbipy.

Table 2. Results obtained by transformation of "living" carbocationic polymerization of IB to "living" radical polymerization

Exp	Monomer	Initiating system	Temp °C	$M_{n,th}$	$M_{n,exp}$	M_w/M_n
1	IB/St	dCuOMe/$TiCl_4$/DTBP	-80	7500	7800	1.31
2	St	dPIB-St-Cl/CuCl/dNbipy	100	13370	13350	1.18
3	MA	dPIB-St-Cl/CuCl/dNbipy	100	11800	12200	1.41
4	MMA	dPIB-St-Cl/CuCl/dNbipy	100	23100	22500	1.45
5	IBA	dPIB-St-Cl/CuCl/dNbipy	100	17270	18850	1.44
6	IB/St	dCuOMe/$TiCl_4$/DTBP	-80	30000	28800	1.31
7	St	dPIB-St-Cl/CuCl/dNbipy	100	48000	48820	1.14
8	MA	dPIB-St-Cl/CuCl/dNbipy	100	32000	31810	1.42
9	MMA	dPIB-St-Cl/CuCl/dNbipy	100	33000	33500	1.47
10	IBA	dPIB-St-Cl/CuCl/dNbipy	100	48000	49500	1.21

Conditions: Exp. 1 $[IB]_o$ =1 mol/L, $[St]_o$= 4.5×10^{-2} mol/L, $[dCuOMe]_o$ = 7.5×10^{-3} mol/L, $[dCuOMe]_o/[TiCl_4]_o/[DTBP]_o$ = 1/25/0.5, CH_2Cl_2/Hexane= 4/6 v solvent, conversion =99.8 %; Exp. 2 $[St]_o$ =2.67 mol/L, $[dPIB\text{-}St\text{-}Cl]_o$ =0.05 mol/L, $[dPIB\text{-}St\text{-}Cl]_o/[CuCl]_o/[dNbipy]_o$ = 1/1/2, $C_6H_5CH_3$ solvent, conversion =98.9 %; Exp.3 $[MA]_o$ =2.32 mol/L, $[dPIB\text{-}St\text{-}Cl]_o$ =0.05 mol/L, $[dPIB\text{-}St\text{-}Cl]_o/[CuCl]_o/[dNbipy]_o$ = 1/1/2, $C_6H_5CH_3$ solvent, conversion =99.2 %; Exp.4 $[MMA]_o$ =7.65 mol/L, $[dPIB\text{-}St\text{-}Cl]_o$ =0.05 mol/L, $[dPIB\text{-}St\text{-}Cl]_o/[CuCl]_o/[dNbipy]_o$ = 1/1/2, $C_6H_5CH_3$ solvent, conversion =97.1 %; Exp.5 $[IBA]_o$ =2.64 mol/L, $[dPIB\text{-}St\text{-}Cl]_o$ =0.05 mol/L, $[dPIB\text{-}St\text{-}Cl]_o/[CuCl]_o/[dNbipy]_o$ = 1/1/2, $C_6H_5CH_3$ solvent, conversion =97.19 %;Exp. 6 $[IB]_o$ =1 mol/L, $[St]_o$= 4.5×10^{-2} mol/L, $[dCuOMe]_o$ = 2×10^{-3} mol/L, $[dCuOMe]_o/[TiCl_4]_o/[DTBP]_o$ = 1/25/0.5, CH_2Cl_2/Hexane= 4/6 v solvent, conversion =99.8 %; Exp. 7 $[St]_o$ =8.7 mol/L, $[dPIB\text{-}St\text{-}Cl]_o$ =0.05 mol/L, $[dPIB\text{-}St\text{-}Cl]_o/[CuCl]_o/[dNbipy]_o$ = 1/1/2, conversion =98.0 %; Exp.8 $[MA]_o$ =1.28 mol/L, $[dPIB\text{-}St\text{-}Cl]_o$ =0.05 mol/L, $[dPIB\text{-}St\text{-}Cl]_o/[CuCl]_o/[dNbipy]_o$ = 1/1/2, $C_6H_5CH_3$ solvent, conversion =99.1 %; Exp.9 $[MMA]_o$ =1.60 mol/L, $[dPIB\text{-}St\text{-}Cl]_o$ =0.05 mol/L, $[dPIB\text{-}St\text{-}Cl]_o/[CuCl]_o/[dNbipy]_o$ = 1/1/2, $C_6H_5CH_3$ solvent, conversion =98.1 %; Exp.10 $[IBA]_o$ =4.74 mol/L, $[dPIB\text{-}St\text{-}Cl]_o$ =0.05 mol/L, $[dPIB\text{-}St\text{-}Cl]_o/[CuCl]_o/[dNbipy]_o$ = 1/1/2, conversion =97.3 %. Please, note that in the earlier publication (Ref. 56), twice lower concentrations of the difunctional initiators and macroinitiators for experiments 1-10 were erroneously reported

The GPC chromatograms of starting Cl-St-PIB-St-Cl and Cl-PSt-b-St-PIB-St-PSt-Cl, triblock copolymer are illustrated in Figure 2. The GPC showed that molecular weight distributions of triblock copolymers were unimodal and narrow. No signal attributed to starting macroinitiators was detected.

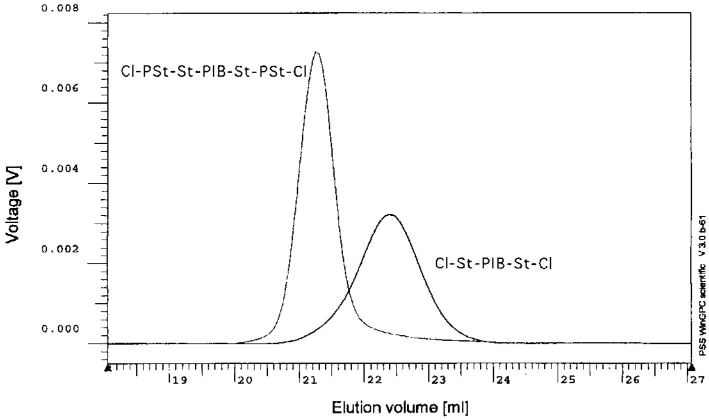


Fig. 2. GPC chromatograms for Cl-St-PIB-St-Cl and Cl-PSt-b-St-PIB-St-b-PSt-Cl polymers shown in Table 1 (exp. 6 and 7)

Thus, a general method of transformation of "living" carbocationic into "living" radical polymerization, without any modification of initiating sites, has been successfully developed for preparation of AB and ABA-block copolymers.

“Living” Cationic Ring Opening Cationic Polymerizatiom (CROP)

In CROP the propagation proceeds by a nucleophilic substitution at the onium ion. The monomers are cyclic ethers (epichlorohydrin, tetrahydrofuran), cyclic acetals (1,3,5-trioxane, 1,3-dioxolane, 1,3-dioxepane), lactones, sulfides, or lactams. Many initiating systems based on carbenium ion salts, triflic acid, anhydride, and esters or Lewis acids were applied for CROP.(Ref. 58).

One of the most studied and best understood systems is CROP of tetrahydrofuran (THF), which proceeds in a "living" fashion. In the presence of triflic derivatives, the equilibrium between oxonium ions and esters is established. It is possible to prepare mono and difunctional polymers and use them for the synthesis of the corresponding diblock and triblock copolymers.

Two examples of synthesis of AB or ABA block copolymers by transformation of "living" CROP into "living" ATRP are shown below. First the polymerization of tetrahydrofuran (THF) with bromopropionyl bromide/AgOTf leads to PTHF which contains bromopropionyl at one end and -OH at the other end (after termination of reaction with H_2O). This PTHF macroinitiator was used for ATRP of styrene or methyl acrylate in order to obtain Br-PSt-b-PTHF-OH or Br-PMA-b-PTHF-OH copolymers.

Scheme 4

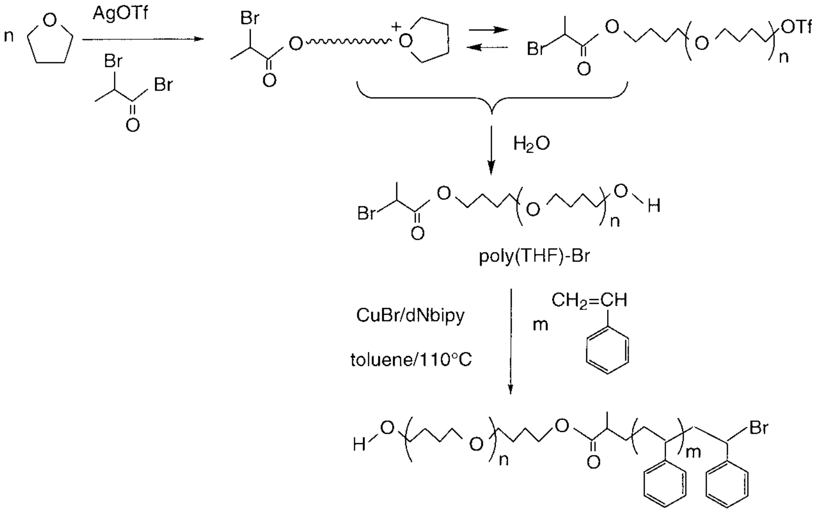


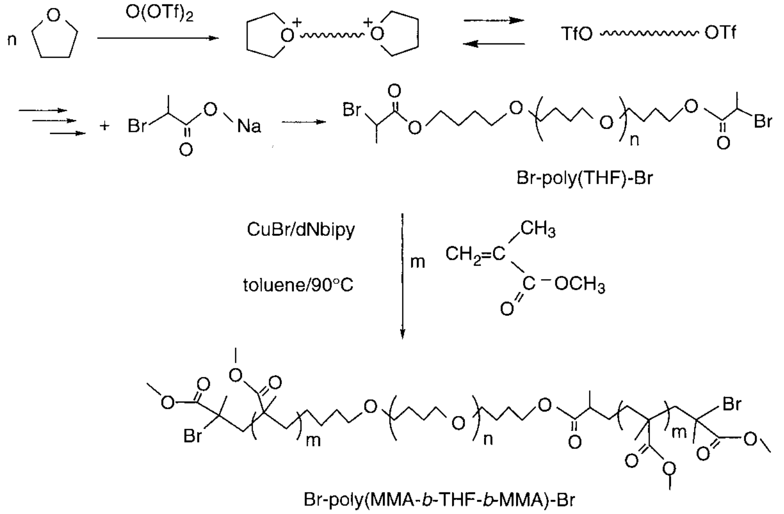
Table 3. Results Obtained by Transformation of Cationic Ring-Opening Polymerization of THF to ATRP

monomer	pTHF-Br/ monomer/ CuBr/dNbipy	temp., °C	$M_{n, th}$	$M_{n, exp}$	ratio of segments (NMR)	M_w/M_n
styrene	1/150/1/2	110	30600	29000		1.55
styrene	1/150/1/2	110	30600	31000	1/1.3	1.46
MMA	1/150/1/2	110	30000	32500		1.75
MMA	1/200/1/2	90	35000	56700	1/1.4	1.21
MA	1/150/1/2	110	27900	93200		2.74
MA	1/200/0.8/1.6	110	32200	62000	1/1.4	1.49
MA	1/150/1/2	90	28000	28500		1.32

initiating system; pTHF-Br/CuBr/dNbipy, poly(THF)-Br: M_n = 15400, M_w/M_n = 1.39, time 24 h, Conv. >97%

Synthesis of ABA block copolymers involved polymerization of THF with difunctional initiator Tf_2O, and then subsequent reaction of the "living" tertiary oxoniun ion end group with sodium bromopropionate to generate a difunctional macroinitiator carrying bromopropionyl groups at both ends (Scheme 5). Formation of triblock copolymers was successful with MMA, demonstrated by the increase of molecular weights from M_n=21 000 (Br-PTHF-Br) to M_n=73 000 (triblock) together with the decrease of polydispersities from M_w/M_n=1.71 to M_w/M_n=1.34. Blocking with styrene and methyl acrylate was, however, much slower and less efficient than with MMA.

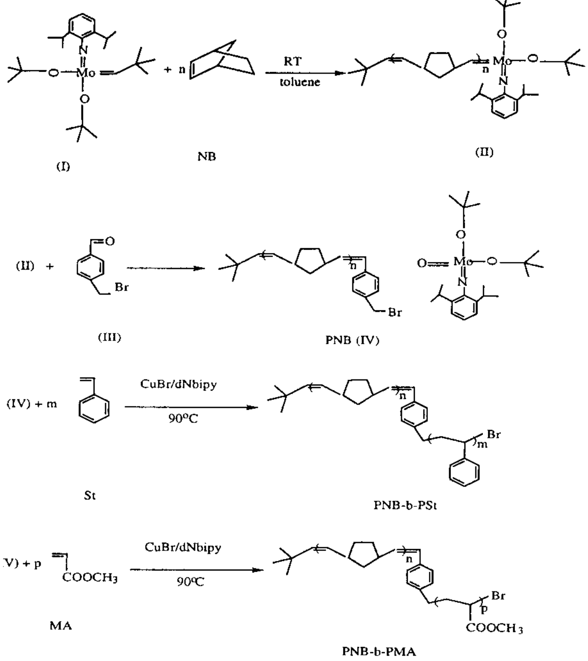
Scheme 5



Ring Opening Metathesis Polymerization (ROMP)

It is possible to prepare "living" (co)polymers by ROMP if the monomer is highly strained (Ref. 10, 11, 59). ROMP proceeds via a [2+2] cycloaddition of a cycloalkene double bond to a metal alkylidene to give a metallacyclobutane intermediate (Ref. 11). An example of synthesis of block copolymers by transformation of "living" ROMP into "living" ATRP is shown in Scheme 6. The well-characterized molybdenum and tungsten alkylidene complexes of type $M(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ (Ar = 2,6-diisopropylphenyl) initiate 'living" polymerization of norbornene (Ref. 11).Norbornene was polymerized rapidly in toluene at room temperature with molybdenum complex (I). After 1/2 h the mixture of living PNB (II) was reacted with 3 equiv. of 4-formylbenzyl bromide (III). A Wittig-like reaction took place and a polynorbornene (IV) with a benzylic bromide at the end was obtained.

Scheme 6



This PNB with benzyl bromine termini was used as initiator for homogeneous ATRP of styrene and methyl acrylate. The same procedure was applied for synthesis of block copolymers based on dicyclopentadiene (DCPD), to prepare PDCPD-b-PSt, PDCPD-b-PMA. The resulting polymers show clear microphase separation and two glass transitions for PNB and PSt or PMA, respectively.

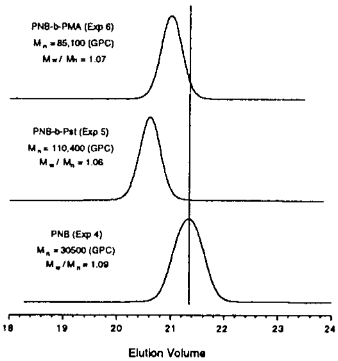


Fig. 3. The GPC traces for PNB-Br and PNB-b-PSt-Br polymers shown in Table 4 (exp. 4-6)

Table 4. Block Copolymers by Transformation of Living ROMP into Controlled/"Living" ATRP

Exp.	**Monomer**	**Initiator**	**Temp. °C**	**$M_{n,th}$**	**M_n, NMR**	**M_n, GPC**	**M_w/M_n**
1	NB	Schrock carbene	RT	5000	5700	12300	1.21
2	St	PNBBr/CuBr/ dNbipy	90		26000	32100	1.16
3	MA	PNBBr/CuBr/ dNbipy	90		12000	18500	1.31
4	NB	Schrock carbene	RT	15000	14500	30500	1.09
5	St	PNBBr/CuBr/ dNbipy	90		95000	110400	1.06
6	MA	PNBBr/CuBr/ dNbipy	90		60000	85100	1.07
7	DCPD	Schrock carbene	RT	5000	7000	12100	1.24
8	St	PDCPDBr/CuBr /dNbipy	90		17000	20100	1.37
9	MA	PDCPDBr/CuBr /dNbipy	90		21000	25300	1.47

Conditions: Exp. 1: $[NB]_0$ = 0.3 mol/L, $[Initiator]_0$ = 8×10^{-3} mol/L, toluene, reaction time = 1h, $[4\text{-bromomethylbenzaldehyde}]_0$ =32×10^{-3} mol/L; Exp. 2: $[St]_0$ = 8.7 mol/L (bulk), $[PNBBr]_0$ = 3×10^{-3} mol/L, $[PNBBr]_0/[CuBr]_0/[dNbipy]_0$ = 1/1/2 mol, time 12 h; Exp. 3: $[MA]_0$ = 4.57 mol/L (toluene), $[PNBBr]_0$ = 3×10^{-3} mol/L, $[PNBBr]_0/[CuBr]_0/[dNbipy]_0$ = 1/1/2 mol, time 12 h; Exp. 4: $[NB]_0$ = 0.3 mol/L, $[Initiator]_0$ = 2.66×10^{-3} mol/L, toluene, time = 1h, $[4\text{-bromomethyl-benzaldehyde}]_0$ =12×10^{-3} mol/L; Exp. 5: $[St]_0$ = 8.7 mol/L (bulk), $[PNBBr]_0$ = 3×10^{-3} mol/L, $[PNBBr]_0/[CuBr]_0/[dNbipy]_0$ = 1/1/2 mol, time 12 h; Exp. 6: $[MA]_0$ = 4.57 mol/L (toluene), $[PNBBr]_0$ = 3×10^{-3} mol/L, $[PNBBr]_0/[CuBr]_0/[dNbipy]_0$ = 1/1/2 mol, time 12 h; Exp. 7: $[DCPD]_0$ = 0.3 mol/L, $[Initiator]_0$ = 8×10^{-3} mol/L, toluene, time = 1h, $[4\text{-bromomethyl benzaldehyde}]_0$ =32×10^{-3} mol/L; Exp. 8: $[St]_0$ = 8.7 mol/L (bulk), $[PDCPDBr]_0$ = 3×10^{-3} mol/L, $[PDCPDBr]_0/[CuBr]_0/[dNbipy]_0$ = 1/1/2 mol, time 12 h; Exp. 9: $[MA]_0$ = 4.57 mol/L (toluene), $[PDCPDBr]_0$ = 3×10^{-3} mol/L, $[PDCPDBr]_0/[CuBr]_0/[dNbipy]_0$ = 1/1/2 mol, time 12 h.

Transformation of step - growth polymerization to ATRP(Ref. 60)

Step - growth polymers with activated halogen end groups were also used as macroinitiators. For example, polysulfone was prepared by the condensation polymerization of 4,4' - difluorosulfone with bisphenol A in slight excess to prepare a polymer with phenolic end groups. Low molecular weight polymers were prepared to more easily discern the end groups by ^1H NMR. The macroinitiator was prepared by treating the polysulfone with 2-bromopropionyl bromide in the presence of pyridine. The degree of functionality appeared to be quite high as the molecular weight determined by GPC (THF, relative to PSt standards, M_n = 4 480, M_n / M_w = 1.5) was in close agreement with that determined by ^1H NMR (M_n = 4 030) through analysis of the end groups.

The ABA block copolymers of polysulfone (B) with either styrene or butyl acrylate (A) were prepared by ATRP. The conversion of the polymerizations after 6.75 hours at 110 °C was found to be: styrene, 67 % and butyl acrylate, 95%. The resulting polymers were confirmed as block copolymers after examination of the SEC traces and ^1H NMR spectra of the polymers.

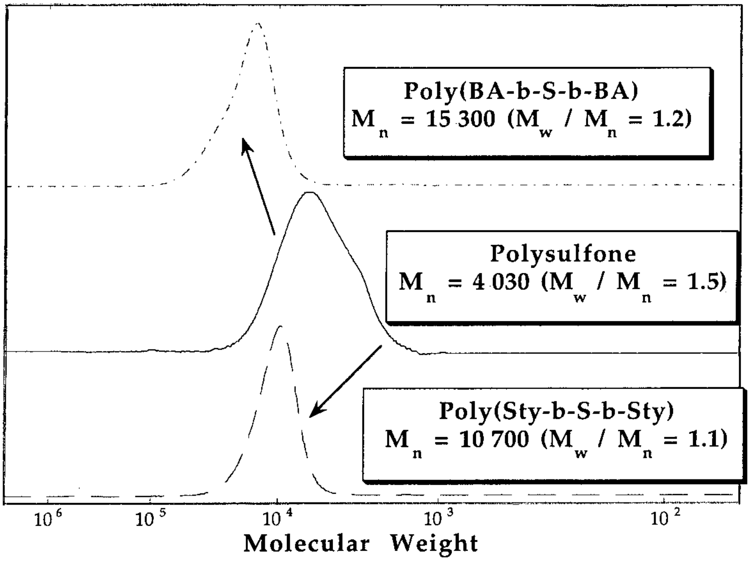


Fig. 4. GPC traces of polysulfone macroinitiator and polysulfone block copolymers with styrene and butyl acrylate

GPC of poly(styrene-b-sulfone-b-styrene) and poly(butyl acrylate-b-sulfone-b-butyl acrylate) showed that the copolymer peaks had shorter retention times than the macroinitiator and therefore had higher molecular weights. It is interesting to note that the molecular weight distributions of the two copolymers were narrower than the initial macroinitiator; styrene: M_w / M_n = 1.1, butyl acrylate: M_w / M_n = 1.2, due to the well defined side blocks prepared by ATRP.

The molecular weights of the copolymers were also estimated by ^{1}H NMR. For the butyl acrylate copolymer, the molar ratio of the -CH_2-OC(O) to the aromatic protons of polysulfone was found to be $r = 11$. The product of r and the degree of polymerization of polysulfone ($DP_B = 8$), yielded the overall degree of polymerization for butyl acrylate ($DP_{2A} = 88$). This is in good agreement with the expected degree of polymerization as defined by $DP = \Delta[BA] / [I]_o = 95$. The total molecular weight of the copolymer was $M_n = 15{,}300$. Similar examination of the ^{1}H NMR spectrum for the styrene copolymer, yielded a total molecular weight of $M_n = 10{,}700$; the degree of polymerization of styrene was $DP_{2A} = 64$, whereas the expected value, assuming quantitative initiation, was $DP = \Delta[St] / [I]_o = 67$.

The physical properties of the two copolymers were quite different from the separate homopolymers. The styrene - sulfone copolymer made very brittle films, which were optically clear. The butyl acrylate - sulfone copolymer produced clear, rubbery films. This contrasts the behavior of low molecular weight butyl acrylate which behaves as a viscous fluid.

The synthesis of well defined block copolymers of a step - growth polymer, polysulfone, and the vinyl monomers styrene and butyl acrylate, has been demonstrated. The macroinitiator was prepared by conversion of the polysulfone's phenol end groups to α-haloesters. This macrointiator was then used to initiate the polymerization of styrene or butyl acrylate by ATRP. The polymerization of the two vinyl monomers was shown to cleanly yield block copolymers with novel physical properties.

Other Systems

In addition to carbocationic, cationic ring-opening, ring-opening metathesis polymerization and step growth systems, several other transformations have been successful. This includes carbanionic polymerization of styrene and dienes terminated in the presence of oxiranes and transformed to the 2-bromoisobutyroxy terminal groups which were successfully used to initiate ATRP of styrene and (meth)acrylates; anionic ROP of hexamethylcyclotrisiloxane terminated with $ClSiMe_2CH_2CH_2PhCH_2Cl$ to initiate ATRP of styrene and acrylates as well as a variety of commercially available polymers such as polychloroprene, Exxpro, i.e., polyisobutene-co-poly(p-bromomethylstyrene) and partially chlorosulfonated polyethylene which have been used directly to start ATRP grafting of well defined polystyrene and poly(meth)acrylates. In addition, polydimethylsiloxane with either pendant or terminal vinyl and Si-H groups has been converted by hydrosilation to ATRP-active benzyl chloride, 2-bromoisobutyroxy or 2-bromopropionoxy groups to form triblock and graft copolymers by ATRP of styrenes and (meth)acrylates.

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