## Block Copolymers by Transformation of Living Ring-Opening Metathesis Polymerization into Controlled/"Living" Atom Transfer Radical Polymerization

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ABSTRACT: A general method of transformation of living ring-opening metathesis polymerization (ROMP) into controlled/"living" atom transfer radical polymerization (ATRP) is reported for the preparation of block copolymers. For example, the macroinitiators PNB– $C_6H_4$ – $CH_2Br$  ( $M_n = 30520$ ,  $M_w/M_n = 1.09$ ) or PDCPD– $C_6H_4$ – $CH_2Br$  ( $M_n = 12100$ ,  $M_w/M_n = 1.24$ ) were prepared by ROMP of norbornene (NB) or dicyclopentadiene (DCPD) and subsequent Wittig-like reactions with *p*-(bromomethyl)benzaldehyde. These compounds were used as efficient macroinitiators for homogeneous controlled/"living" ATRP to prepare block copolymers with styrene (St), PNB-*b*-PSt ( $M_n = 110400$ ,  $M_w/M_n = 1.06$ ) and PDCPD-*b*-PSt ( $M_n = 20100$ ,  $M_w/M_n = 1.37$ ), and methyl acrylate (MA), PNB-*b*-PMA ( $M_n = 85100$ ,  $M_w/M_n = 1.07$ ) and PDCPD-*b*-PMA ( $M_n = 25300$ ,  $M_w/M_n = 1.47$ ).

Living or controlled/"living" polymerization<sup>1</sup> techniques allow the synthesis of well-defined polymers with controlled molecular weight, polydispersities, and terminal functionalities. In these systems the contribution of chain-breaking reactions is absent or insignificant,<sup>2</sup> the polymerization proceeds until all of the monomer has been consumed, and further additions of monomer result in continued polymerization. Living or controlled/ "living" polymerization can proceed by anionic,<sup>3</sup> cationic,<sup>2,4</sup> group transfer,<sup>5</sup> metathesis,<sup>6</sup> Ziegler-Natta,<sup>7</sup> or radical mechanisms.<sup>8</sup> These polymerization techniques give several powerful tools for the synthesis of block copolymers with well-defined structures: (a) sequential monomer addition, (b) coupling of living chains, (c) transformation of a growing chain end to a group capable of initiating polymerization of the second monomer.<sup>9</sup> The latter method is especially well-suited for block copolymers prepared from monomers which polymerize by two different mechanisms.

The recent developments in ring-opening metathesis polymerization (ROMP) have opened new synthetic routes to a variety of well-defined polymers.<sup>6,10</sup> Welldefined complexes based on Ti,<sup>11</sup> Mo,<sup>12</sup> W,<sup>13</sup> Ta,<sup>14</sup> Re,<sup>15</sup> and Ru,<sup>16</sup> which are able to initiate living ROMP, have been developed. The combination of monomers which may be converted into block copolymers by living ROMP is limited to highly strained cycloolefins, e.g., norbornene, norbornadiene, dicyclopentadiene, or other strained polycyclics for which ring opening is essentially irreversible.<sup>17</sup> It therefore seems that the range of attainable block copolymers would be greatly extended if, after polymerization of the first monomer, a convenient process is divised by which the mechanism of propagation is changed to one best suited to the propagation of the second monomer.<sup>18</sup> Grubbs reported block copolymer synthesis by changing the mechanism from living ROMP of cycloalkene to aldol group transfer polymerization of silyl vinyl ether<sup>19</sup> and from ROMP of norbornene to Ziegler-Natta polymerization of ethylene.20

In the last few years many efforts have been devoted to development of controlled/"living" radical polymeri-

zation. Inifer or iniferter methodology,<sup>8a</sup> stable free radicals such as TEMPO,<sup>8b,c</sup> various organometallic species,<sup>21</sup> degenerative transfer,<sup>22</sup> and atom transfer radical polymerization (ATRP)<sup>8d-f</sup> were developed. ATRP seems to be the most robust of these systems. The extension of atom transfer radical addition<sup>23</sup> to ATRP provides a new and efficient way to conduct a controlled/ <sup>\*</sup>living" radical polymerization.<sup>8d</sup> 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(s), ATRP of vinyl monomers such as styrene, acrylates, methyl methacrylate, acrylonitrile, and isobutene, proceeds in a controlled/ "living" fashion.<sup>8d,24</sup> The resulting polymers have a degree of polymerization predetermined by  $\Delta[M]/[I]_0$  up to  $M_n \approx 10^5$  and low polydispersity,  $1.1 < M_w/M_n < 1.5$ . For example, when an alkyl bromide, 1-PhEtBr, is used as the initiator, and CuBr/4,4'-diheptyl-2,2'-bipyridine or CuBr/4,4'-di(5-nonyl)-2,2'-bipyridine is used as the catalyst, styrene is polymerized by repetitive atom transfer radical additions to yield a well-defined, high molecular weight polymer, with a narrow molecular weight distribution  $(\dot{M}_w/M_n = 1.05)$ .<sup>25</sup>

$$P_{n}-X + Cu^{I}/2L \xrightarrow{k_{act}} P_{n} + Cu^{II}X/2L$$

$$\begin{pmatrix}k_{p}\\k_{p}\end{pmatrix}$$
monomer

Recently, we reported a general method of transformation of "living" carbocationic polymerization into controlled/"living" ATRP without any modification of chain ends and the successful preparation of AB and ABA-block copolymers.<sup>26</sup> The synthesis of block and graft copolymers by combination of living ring-opening metathesis polymerization with controlled/"living" ATRP has not yet been reported. This paper is focused on a transformation technique for making block copolymers involving monomers polymerizable by ring-opening metathesis and radical mechanisms. We describe here that polynorbornene (PNB) and poly(dicyclopentadiene) (PD-CPD) synthesized by living ROMP, capped with benzyl bromide are efficient initiators for controlled/"living" ATRP of styrene (St) or methyl acrylate (MA) leading to PNB-*b*-PSt, PNB-*b*-PMA, PDCPD-*b*-Pst, and PDCPD*b*-PMA copolymers, as shown in Scheme 1.

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Scheme 1



A well-characterized Mo-alkylidene complex Mo- $(CHCPhMe_2)(NAr)(O-t-Bu)_2$  (Ar = 2,6-diisopropylphenyl)<sup>27</sup> was chosen as the initiator in living ROMP. The polymerization of NB initiated by this complex at room temperature proceeds in a living process. Thus, it displays clean first-order kinetics in the monomer, a linear increase of molecular weight with monomer conversion, and leads to polymers with low polydispersities in agreement with the absence of chain termination and transfer steps, and the rate constant of initiation being equal/greater than that of propagation. In the first step NB or endo-DCPD were polymerized by ROMP. The polymerizations were carried out at room temperature with Mo complex (I) in toluene as a solvent. The resulting Mo-carbene ended polymer (II) was reacted with p-(bromomethyl)benzaldehyde (III) in a Wittig-type reaction to produce polymer containing benzyl bromide at the chain end.<sup>28</sup> p-(Bromomethyl)benzaldehyde was prepared as described in the literature.<sup>29</sup> After recovery by precipitation in methanol, the polymer was characterized by GPC and <sup>1</sup>H-NMR. The experimental number average molecular weight  $M_{n,exp}$ 

was double to that of the theoretical one,  $M_{\rm n,th}$ , when polystyrene standards were used for GPC calibrations. Katz has previously reported that  $M_{\rm n,SEC}$  be divided by 2.0 to obtain the actual  $M_{\rm n}$  for polynorbornene when polystyrene calibration was used.<sup>30</sup>  $M_{\rm n,th}$  was calculated by means of eq 1:

$$M_{\rm n,th} = ([M]_0/[\text{Initiator}]_0)(\text{MW})_0 \text{ (conversion)} (1)$$

The molecular weight distribution was narrow ( $M_w/M_n$  = 1.21) (experiment 1). The number average molecular weight determined by <sup>1</sup>H-NMR was close to the theoretical one,  $M_{n,th}$ . The end group analysis by <sup>1</sup>H-NMR (Figure 1) showed that the PNB contained the R-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>Br terminal group. The PNB and PDCPD with terminal benzyl bromide functionalities were used as macroinitiators in controlled/"living" ATRP. ATRP exhibits all of the experimental criteria of a controlled/ "living" polymerization and is a general method for a large number of radically polymerizable monomers. Thus PNB and PDCPD with benzyl bromide chain ends, PNB-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>Br and PDCPD-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>Br, were



**Figure 1.** <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>) of PNB–Br polymers  $[M_n \text{ (GPC)} = 12 300, M_w/M_n = 1.21, M_n \text{ (NMR)} = 5700].$ 

used to initiate homogeneous block ATRP of styrene, and methyl acrylate in the presence of a catalyst based on CuBr and 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbipy). Table 1 summarizes polymerization results in ROMP of NB (experiments 1 and 4), DCPD (experiment 7), then homogeneous ATRP of styrene (St) (experiments 2 and 5 for initiation with PNB; experiment 8 for initiation with PDCPD), and methyl acrylate (MA) (experiments 3 and 6 for initiation with PNB; experiment 9 for initiation with PDCPD).

The GPC chromatograms of starting  $PNB-C_6H_4-CH_2Br$  (experiment 4) and the PNB-b-PSt-Br (experiment 5), PNB-b-PMA-Br (experiment 6) copolymers are illustrated in Figure 2. The clear shift of molecular weights without any shoulder indicates clean formation of block copolymers.

The structure of block copolymers was analyzed by <sup>1</sup>H-NMR spectroscopy. Figure 3 illustrates 300 MHz <sup>1</sup>H-NMR spectra of the PNB-*b*-PSt–Br (experiment 2) copolymer and demonstrates the presence of both blocks



**Elution Volume** 

**Figure 2.** The GPC chromatograms for PNB–Br and PNB*b*-PSt–Br polymers shown in Table 1 (experiments 4, 5, and 6).

derived from NB and St. Also the disappearance of the signal from benzylic protons at 4.4 ppm supports the consumption of the bromine intiating group. The ratio of incorporated monomer units was determined by integration of the proton at the double bond from PNB and the aromatic protons from PSt.

Data for the DSC analysis of the PNB-*b*-PSt, PNB*b*-PMA, and PNB are presented in Table 2. Phase separation occurs in all copolymers, and two glass transitions are observed. For example PNB-*b*-PSt and PNB-*b*-PMA had  $T_g = 45$  °C for PNB and  $T_g = 95$  °C and 7 °C for the St and MA block, respectively.

In conclusion, we report a general method of transformation of living ROMP into controlled/"living" ATRP and the successful preparation of block copolymers. We have demonstrated that PNB $-C_6H_4-CH_2Br$  or PD-CPD $-C_6H_4-CH_2Br$  prepared by ROMP and subsequent Wittig-like reactions with *p*-(bromomethyl)benzaldehyde were used as efficient macroinitiators for homogeneous controlled/"living" ATRP of styrene and methyl acrylate. This procedure is now being tested for other monomers

Table 1. Block Copolymers by Transformation of Living ROMP into Controlled/"Living" ATRP<sup>a</sup>

exp	monomer	initiator	temp, °C	$M_{ m n,th}$	<i>M</i> <sub>n</sub> , NMR	M <sub>n</sub> , GPC	$M_{\rm w}/M_{\rm n}$
1	NB	Schrock carbene	rt	5000	5700	12 300	1.21
2	St	PNBBr/CuBr/dNbipy	90		26 000	32 100	1.16
3	MA	PNBBr/CuBr/dNbipy	90		12 000	18 500	1.31
4	NB	Schrock carbene	rt	15 000	14 500	30 500	1.09
5	St	PNBBr/CuBr/dNbipy	90		95 000	110 400	1.06
6	MA	PNBBr/CuBr/dNbipy	90		60 000	85 100	1.07
7	DCPD	Schrock carbene	rt	5000	7000	12 100	1.24
8	St	PDCPDBr/CuBr/dNbipy	90		17 000	20 100	1.37
9	MA	PDCPDBr/CuBr/dNbipy	90		21 000	25 300	1.47

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



**Figure 3.** <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>) of PNB-*b*-PSt-Br copolymer [ $M_n$  (GPC) = 32 100,  $M_w/M_n$  = 1.16,  $M_n$  (NMR) = 26 000].

 Table 2. DSC Analysis of Homopolymers and Block

 Copolymers

polymer	M <sub>n</sub> (A) NMR	M <sub>n</sub> (B) NMR	T <sub>g</sub> (A), °C DSC	T <sub>g</sub> (B), °C DSC
PNB	5 700		32	
PNB	14 500		33	
PNB- <i>b</i> -Pst	5 700	20 000	42	94
PNB-b-PSt	14 500	80 000	45	95
PNB- <i>b</i> -PMA	5 700	6 300	40	7
PNB- <i>b</i> -PMA	14 500	45 000	41	12

and also for the synthesis of the corresponding triblock copolymers.

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**Supporting Information Available:** Experimental section including general procedures of homopolymerization and block copolymerization and (co)polymer characterization; <sup>1</sup>H-NMR spectra of PDCPD–Br polymer (experiment 7) [Figure S1], <sup>1</sup>H-NMR spectra of PNB-*b*-PMA–Br copolymer (experiment 3) [Figure S2], <sup>1</sup>H-NMR spectra of PDCPD-*b*-PSt–Br (experiment 8) [Figure S3], and <sup>1</sup>H-NMR spectra of PDCPD-*b*-PMA–Br (experiment 9) [Figure S4]; GPC chromatograms for PNB–Br and PNB-*b*-PSt–Br polymers (experiments 1 and 2) [Figure S5], GPC chromatograms for PDCPD–Br and PDCPD-*b*-PSt–Br (experiments 7 and 8) [Figure S6], GPC chromatograms for PDCPD–Br and PDCPD-*b*-PMA–Br (experiments 7 and 9) [Figure S7] (10 pages). Ordering information is found on any current masthead page.

## **References and Notes**

(1) (a) Living and controlled/"living" polymerizations should be distinguished. The living polymerization can be defined as a chain growth process in which no irreversible chain transfer or termination exists. The controlled/"living" polymerization is the polymerization system which provides well-defined polymers but allows tolerable amounts of chain transfer or termination. (b) Matyjaszewski, K.; Muller, A. H. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 6.

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