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Atom Transfer Radical Polymerization of Tulipalin A: A Naturally Renewable Monomer

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Natural products are renewable, environmentally friendly, biocompatible, and biodegradable, and they may also possess some special physical and biomedical properties. Recently, a possibility of using natural products to replace petroleum-based raw materials in large commodity markets, such as plastics, fibers, and fuels, has been broadly studied.^{1,2} For example, several compounds containing an α -methylene- γ -butyrolactone moiety were found and isolated from various plants.^{3–6} The simplest member of these butyrolactones, tulipalin A (α -methylene- γ -butyrolactone) (MBL), found in tulips, is the most studied monomer and has already successfully been polymerized by radical mechanism (using AIBN),^{7–9} by group-transfer polymerization,¹⁰ and by photocopolymerization with methoxystyrene.¹¹ MBL consists of a five-member ring with an oxygen and carbonyl group, possesses structural features similar to those of methyl methacrylate, and polymerizes in a similar manner. The reactivity of MBL in radically initiated polymerization was found to be a little higher than that of methyl methacrylate because of the planar structure of MBL.¹² The planarity favors delocalization of the chain-end radical's spin density and reduces steric hindrance. The resulting polymers are more rigid than other polymethacrylates.¹³ Poly(α -methylene- γ -butyrolactone) (PMBL) has good durability, a high refractive index (1.540),¹⁴ and high T_g (195 °C).⁷ Various copolymers and blends containing MBL units have good optical properties, heat, weathering, scratch, and solvent resistance.¹⁵ Although various polymerization techniques have been used for

the polymerization of MBL, there is no report on conducting a controlled radical polymerization of MBL. Here we report the first preparation of a well-defined homopolymer of MBL using atom transfer radical polymerization.^{16–23} The preparation of well-defined diblock and triblock copolymers of MBL is also presented.

MBL was polymerized using CuBr with 2,2'-bipyridine (bpy) as a catalyst complex and bromopropionitrile (BPN) as initiator. A small amount of CuBr₂ was added to the system at the beginning of the reaction to increase the rate of deactivation of radicals initially formed from the initiator. DMF was chosen as the solvent because of poor solubility of PMBL in common solvents. It was found that MBL polymerized rapidly under these conditions, and after 100 min monomer conversion was already 90%. The polymerization was well controlled, and a polymer with predeterminable molecular weight and narrow molecular weight distribution was obtained (Table 1 and Supporting Information, Figure S1). Although at 90% of MBL conversion GPC gave a slightly lower molecular weight than the theoretical value, the molecular weight calculated from ¹H NMR spectra was in good agreement with the predicted value (Table 1).

Then, the preparation of block copolymers containing MBL was investigated. First, a PMBL macroinitiator, with lower molecular weight $M_n = 9600$ g/mol, was chain extended with butyl acrylate. The chain extension was carried out in DMF with CuBr/*N,N,N',N'',N''*-pentamethyldiethylenetriamine (PM-DETA) as a catalyst. Since the solubility of PMBL is poor, the polymer partially precipitated out of the solution after addition of BA monomer. More DMF was added to dissolve the precipitated polymer; however, during the chain extension of the PMBL macroinitiator with BA, the GPC trace showed a bimodal distribution, indicating that only a fraction of the PMBL was chain extended (Supporting Information, Figure S2). This was attributed to the limited solubility of the PMBL macroinitiator in the solvent–monomer mixture.

Because of the low solubility of PMBL, the opposite method for the preparation of block copolymers—extension of various macroinitiators with MBL—was investigated. As the radical reactivity of MBL is high, halogen exchange was used for the ATRP to provide for higher, or at least equal, rate of initiation, in comparison with rate of propagation.²⁴ First, because there should be only a small difference in the reactivities of MBL

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Table 1. Experimental Conditions of ATRP of MBL and Characterization of Prepared Polymers

monomer	initiator	catalyst	ligand	solvent	time	conv ^c (%)	$M_{n,theor}$	$M_{n,exp}$	M_w/M_n
MBL	BPN	CuBr/CuBr ₂	bpy	DMF	100 min	89	21 090	18 200 ^a	1.09
240	1	0.4/0.1	1	40 vol %				(21 100) ^c	
MBL	PMMA-Br	CuCl/CuCl ₂	bpy	DMF	7.5 h	77	15 800	14 900 ^a	1.14
100	1	0.8/0.2	2	55 vol %				(14 800) ^c	
MBL	PBA-Br	CuCl/CuCl ₂	bpy	DMF	44 h	59	31 380	34 100 ^b	1.12
200	1	0.8/0.2	2	52 vol %				(31 100) ^c	
MBL	Br-PBA-Br ^d	CuCl/CuCl ₂	bpy	DMF	11 h	91	38 660	43 700 ^b	1.11
125	1	2.2/0.2	2.4	55 vol %				(39 500) ^c	
MBL	Br-PBA-Br ^d	CuCl/CuCl ₂	bpy	DMF	4 h	45	30 810	31 800 ^c	1.09
75	1	2.2/0.2	2.4	45 vol %					
MBL	Br-PBA-Br ^d	CuCl/CuCl ₂	bpy	DMF	15 h	95	34 490	34 600 ^c	1.11
75	1	2.2/0.2	2.4	45 vol %					
MBL	Br-PBA-Br ^e	CuCl/CuCl ₂	bpy	DMF	7 h	33	54 510	54 100 ^c	1.10
195	1	2.2/0.2	2.4	45 vol %					
MBL	Br-PBA-Br ^e	CuCl/CuCl ₂	bpy	DMF	22 h	65	60 630	62 400 ^c	1.12
195	1	2.2/0.2	2.4	45 vol %					

^a Based on GPC using PMMA standards. ^b Based on GPC using PS standards. ^c Based on ¹H NMR spectra. ^d $M_n = 27\,500$ g/mol, $M_w/M_n = 1.07$ based on GPC using PS standards. ^e $M_n = 48\,200$ g/mol, $M_w/M_n = 1.08$ based on GPC using PS standards.

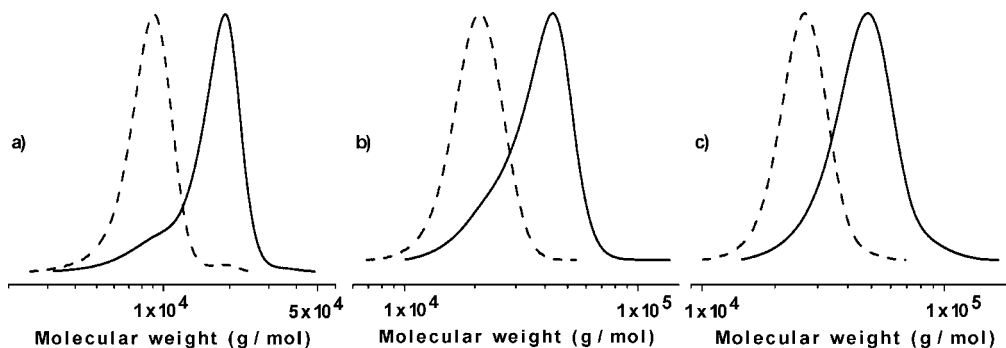


Figure 1. GPC traces during ATRP of MBL. (a) Chain extension from PMMA-Br, (---) PMMA-Br macroinitiator ($M_n = 8250$ g/mol; $M_w/M_n = 1.08$) and (—) PMMA-*b*-PMBL copolymer ($M_n = 14\,900$ g/mol; $M_w/M_n = 1.14$). Experimental conditions: MBL/PMMA-Br/CuCl/CuCl₂/bpy = 100/1/0.8/0.2/2; [MBL] = 2.4 M; $T = 50$ °C, in DMF (55 vol %). (b) Chain extension from PBA-Br, (---) PBA-Br macroinitiator ($M_n = 19\,800$ g/mol; PDI = 1.07) and (—) PBA-*b*-PMBL copolymer ($M_n = 34\,100$ g/mol; PDI = 1.12). Experimental conditions: MBL/PBA-Br/CuCl/CuCl₂/bpy = 200/1/0.8/0.2/2; [MBL] = 2.64 M; $T = 50$ °C, in DMF (52 vol %). (c) Chain extension from Br-PBA-Br, (—) Br-PBA-Br macroinitiator ($M_n = 27\,500$ g/mol; $M_w/M_n = 1.07$) and (---) PMBL-*b*-PBA-*b*-PMBL copolymer ($M_n = 39\,500$ g/mol; $M_w/M_n = 1.11$). Experimental conditions: MBL/Br-PBA-Br/CuCl/CuCl₂/bpy = 125/1/2.2/0.2/2.4; [MBL] = 1.5 M; $T = 50$ °C, in DMF (55 vol %).

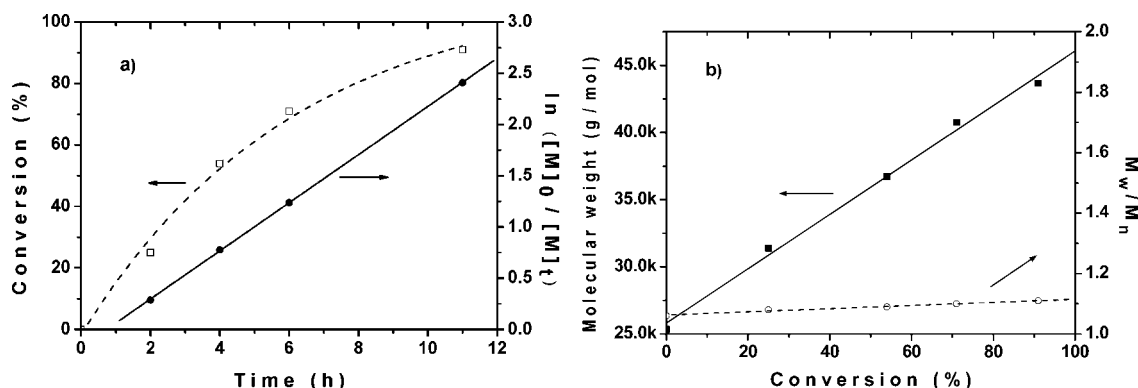


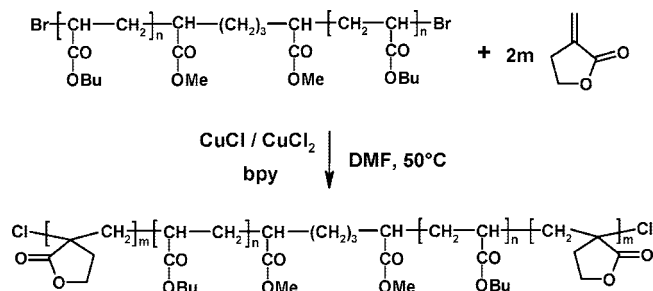
Figure 2. (a) Kinetics and (b) evolution of molecular weight and M_w/M_n with conversion of MBL during chain extension from Br-PBA-Br. Experimental conditions: MBL/Br-PBA-Br/CuCl/CuCl₂/bpy = 125/1/2.2/0.2/2.4; [MBL] = 1.5 M; $T = 50$ °C, in DMF (55 vol %).

and MMA, the chain extension of PMMA with MBL was studied. The reaction, carried out in DMF using a CuCl/CuCl₂/bpy catalyst system, was well controlled, and a block copolymer with predictable molecular weight and narrow molecular weight distribution was prepared (Table 1, Figure 1a, and Supporting Information, Figure S3a).

The extension of PBA with MBL was performed under the same conditions. Although the initiation rate from a PBA-Br macroinitiator should be much lower than the propagation rate of MBL, the halogen exchange ATRP system was efficient enough to achieve a well-controlled chain extension of PBA.

Molecular weights of the obtained block copolymers were in a good agreement with the theoretical values. Copolymers with narrow molecular weight distribution were obtained (Table 1, Figure 1b, and Supporting Information, Figure S3b).

The physical properties of PMBL can be beneficial for some applications. For example, high T_g (195 °C)⁷ of PMBL and its limited solubility can be used for thermoplastic elastomers. Therefore, the synthesis of such a triblock copolymer with soft PBA segment was investigated. The triblock copolymer was prepared by chain extension of a difunctional PBA macroinitiator by MBL (Scheme 1). The chain extension polymerization

Scheme 1. Preparation of PMBL-*b*-PMMA-*b*-PMBL Copolymer

was well controlled, and a copolymer with narrow molecular weight distribution was prepared (Table 1 and Figures 1c and 2). Differences between apparent molecular weight based on GPC and theoretical values (Table 1) could be due to the calibration with linear PS standards. The molecular weight of the copolymer after precipitation was also determined by ^1H NMR in DMF and was in a good agreement with a theoretical value.

In conclusion, homopolymers of α -methylene- γ -butyrolactone with predictable molecular weight and a narrow molecular weight distribution were prepared by atom transfer radical polymerization. Well-defined diblock and triblock copolymers were prepared by chain extension of various macroinitiators, such as poly(methyl methacrylate) and poly(*n*-butyl acrylate), with α -methylene- γ -butyrolactone. Their properties are currently under investigation.

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Supporting Information Available: General procedures for polymerizations and measurements conditions; figure of evolution of molecular weight and M_w/M_n with monomer conversion during

homopolymerization of MBL; figure of GPC traces during chain extension of PMBL-Br with BA; figure of evolution of molecular weight and M_w/M_n with conversion of MBL during chain extension from PMMA-Br and PBA-Br; ^1H NMR spectra of synthesized macroinitiators. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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