

Tailored Synthesis of Structurally Defined Polymers by Organotellurium-Mediated Living Radical Polymerization (TERP): Synthesis of Poly(meth)acrylate Derivatives and Their Di- and Triblock Copolymers

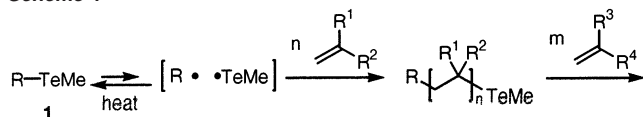
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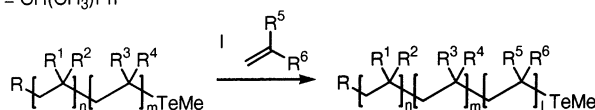
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The synthesis of new nanostructural organic materials by controlled polymerization has attracted a great deal of attention, because these materials would lay essential foundations for nanoscience and nanotechnologies.¹ Living radical polymerization (LRP) is becoming increasingly important for this goal because of its potential applicability to different types of monomers with various polar functional groups, which do not lend themselves to ionic and metal-catalyzed polymerization conditions. While impressive developments in LRP systems have emerged such as nitroxide-mediated polymerization (NMP),² atom transfer radical polymerization (ATRP),³ and reversible addition–fragmentation chain transfer (RAFT),⁴ the invention of a more versatile system is clearly needed. The application of the current LRP system to block copolymer synthesis is severely limited, and suffers from the requirement for care in the order of monomer addition⁵ (Scheme 1). Therefore, a system that allows flexible synthesis of structurally defined block copolymers composed of different families of monomers would offer greater opportunities for the synthesis of organic nanomaterials with new or improved properties.⁶

Scheme 1



a: R = C(CH₃)₂CO₂Et
b: R = CH(CH₃)Ph



We report here a highly versatile method for the synthesis of block copolymers based on organotellurium-mediated living radical polymerization (TERP).^{7,8} We have found that TERP is extremely general and can polymerize different families of monomers, such as styrenes,⁷ acrylates, and methacrylates, using the same initiators in a highly controlled manner. Furthermore, the versatility of TERP allows the synthesis of various AB-, ABA-, and ABC-block copolymers starting from a single monofunctional initiator, regardless of the order of monomer addition.

Before attempting block copolymer synthesis, we first examined the polymerization of acrylates and methacrylates to understand the generality of TERP. Thus, the bulk polymerization of methyl acrylate (MA, 100 equiv) was carried out with the initiators **1**, which are excellent initiators for the polymerization of styrene derivatives,

Table 1. Synthesis of Poly(meth)acrylate Derivatives^a

entry	initiator	monomer ^b	conditions (°C/h)	yield (%)	<i>M_n</i> ^c	PD ^e
1	1a	MA	100/24	70	6400	1.11
2	1b	MA	100/24	86	8800	1.12
3	1b	nBA	100/24	89	10300	1.13
4	1a	tBA	100/24	85	9800	1.18
5 ^d	1b	DMAEA	100/96	81	12000	1.23
6	1b	DMA	105/23	100	10100	1.22
7 ^d	1b	AN	100/24	53	20800	1.07
8	1a	MMA	80/15	67	11800	1.77
9 ^e	1a	MMA	80/13	84	8200	1.16
10 ^e	1b	MMA	80/13	92	9700	1.18
11 ^{e,f}	1b	MMA	80/19	83	16200	1.14
12 ^{g,h}	1b	MMA	80/18	79	36300	1.18
13 ^{g,i}	1b	MMA	80/24	83	79400	1.14
14 ^e	1a	EMA	105/2	97	10600	1.12
15 ^{d,e}	1a	HEMA	80/17	97	22300	1.18

^a Bulk polymerization was carried out by heating the initiator and 100 equiv of monomer under a nitrogen atmosphere. ^b MA: methyl acrylate, nBA: *n*-butyl acrylate, tBA: *tert*-butyl acrylate, DMAEA: 2-dimethylaminoethyl acrylate, DMA: *N,N*-dimethylacrylamide, AN: acrylonitrile, MMA: methyl methacrylate, EMA: ethyl methacrylate, HEMA: 2-hydroxyethyl methacrylate. ^c Molecular weight (*M_n*) and polydispersity (PD) were calibrated by size-exclusion chromatography using polyMMA standards for crude samples. Polystyrene standards were used for entry 7. ^d The reaction was carried out in DMF. ^e 1 equiv of (MeTe)₂ was added. ^f 200 equiv of MMA was used. ^g 2 equiv of (MeTe)₂ was added. ^h 500 equiv of MMA was used. ⁱ 1000 equiv of MMA was used.

by heating at 100 °C for 24 h. We found that both **1a** and **1b** worked efficiently and afforded polyMA with predictable molecular weight (*M_n*) and low polydispersity (PD) (Table 1, entries 1 and 2). The initiators also polymerized a variety of acrylate derivatives efficiently (entries 3–7). It is worth noting that all the monomers gave the desired polymers with low polydispersity (PD < 1.23) and in high yield. The successful polymerization of 2-dimethylaminoethyl acrylate (DMAEA), *N,N*-dimethyl acrylamide (DMA), and acrylonitrile (AN) is particularly noteworthy, since the polar functional groups of these monomers often disturb the precise control of the polymerization using other methods.

We next examined the polymerization of methyl methacrylate (MMA, 100 equiv), but initial attempts revealed that the control of the reaction was insufficient (PD = 1.77, entry 8). The result could be attributed to the high reactivity of MMA toward the polymer-end radicals, and we anticipated that the addition of an agent to cap the radical species would enhance controllability. Because ditellurides are excellent radical-capturing reagents,⁹ they would serve as capping reagents for polymer-end radicals. Indeed, polyMMA with a low polydispersity was obtained by the addition of 1 equiv of (MeTe)₂ (PD = 1.16–1.18, entries 9 and 10). Because the reaction proceeds in a living manner, the molecular weight increased predictably with the amount of MMA used, and high-

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Scheme 2

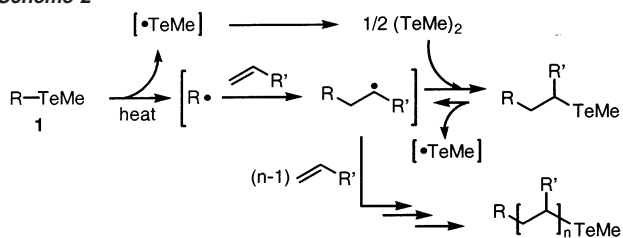


Table 2. Synthesis of AB Di- and ABA Tri- and ABC Triblock Copolymers Using Macroinitiators

entry	macroinitiator ^a	M_n /PD ^b	monomer ^c	yield (%)	M_n /PD ^b
AB Diblock Copolymer					
1	PolySt	9000/1.15	MMA ^d	85	13900/1.25
2	PolySt	9000/1.15	tBA	50	11300/1.18
3	PolyMMA	8500/1.12 ^e	St	85	18800/1.13
4	PolyMMA	8500/1.12 ^e	tBA	57	17100/1.11
5	Poly(tBA)	9600/1.10 ^e	St	77	19200/1.32
6	Poly(tBA)	8200/1.19 ^e	MMA ^d	88	19500/1.35
ABA Triblock Copolymer					
7	PolyMMA- <i>b</i> -polySt	18700/1.18	MMA ^d	85	28100/1.22
8	PolyMMA- <i>b</i> -poly(tBA)	11000/1.11	MMA ^d	83	18600/1.30
ABC Triblock Copolymer					
9	PolySt- <i>b</i> -polyMMA	12600/1.30	tBA	32	16100/1.27
10	PolyMMA- <i>b</i> -polySt	19000/1.13	tBA	45	21800/1.18
11	PolyMMA- <i>b</i> -poly(tBA)	11500/1.09	St	69	21600/1.27

^a The macroinitiator was prepared from **1b** and the corresponding monomer according to the conditions shown in Table 1 (see also Supporting Information). ^b Molecular weight (M_n) and polydispersity (PD) were calibrated by size-exclusion chromatography using polySt standards for crude samples. St: styrene. 100 equiv and 200 equiv of monomers were used for the diblock and triblock copolymer synthesis, respectively. ^d 1 equiv of (MeTe)₂ was added. ^e Calibrated using polyMMA standards.

molecular-weight polyMMA formed with precise molecular weight control by the addition of 2 equiv of (MeTe)₂ (entries 11–13). 2-Hydroxyethyl methacrylate (HEMA) could also be polymerized in the presence of (MeTe)₂ in a highly controlled manner (entry 15).

The effect of the dimethyl ditelluride strongly suggests that the current polymerization proceeds via the ditelluride-capping mechanism as shown in Scheme 2; the tellurium radical generated by the bond homolysis of **1** forms dimethyl ditelluride,¹⁰ which serves as the capping reagent of the polymer end radicals. Increasing the amount of (MeTe)₂ facilitates the formation of the dormant species, thus avoiding further uncontrollable propagation reactions from the polymer end radicals. However, other possibilities involving the degenerative transfer could not be rigorously excluded.¹¹

The previous⁷ and current results suggest that the TERP process would be suitable for a tailored synthesis of block copolymers using macroinitiators, because the same initiators can control the polymerization of different types of monomers under similar thermal conditions. Indeed, the AB diblock copolymer of styrene and MMA could be efficiently prepared starting from either the polystyrene block, which was prepared by **1b** and styrene, or the polyMMA block, which was prepared by **1b** and MMA, with MMA or styrene, respectively (Table 2, entries 1 and 3). We were also able to synthesize block copolymers of styrene and tBA, and of MMA and tBA, regardless of the order of first and second monomers (entries 2 and 4–6). The desired diblock copolymers were obtained in all cases with predictable molecular weight with low polydispersity. Due to the stronger C–Te bond in poly(tBA) compared with the one in polystyrene and polyMMA, the controllability of the diblock

copolymers initiated by the poly(tBA) macroinitiator was slightly less efficient (entries 5 and 6) but is still at an acceptable level.

Because the order of monomer addition is less important in TERP compared to that of other LRP systems, ABA and ABC triblock copolymers could also be prepared starting from diblock macroinitiators (entries 7–11). These triblock copolymers were also obtained in all cases in a highly controlled manner. As an analogy to the successful synthesis of the diblock and triblock copolymers in Table 2, combined with the data in Table 1, various combinations of multiblock copolymers could possibly be synthesized. In addition, end-group transformations of the polymer would also add new functions to the polymers (see Supporting Information). Such possibilities are now under investigation.

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Supporting Information Available: Typical experimental procedures, end-group transformation and preparation of block copolymers (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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