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Stereospecific Anionic Polymerization of Methyl Bicyclobutane-1-carboxylate

Tatsuki Kitayama,*,† Takehiro Kawauchi,† Xiao-Ping Chen,‡ Anne Buyle Padias,‡ and Henry K. Hall, Jr.‡

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan; and Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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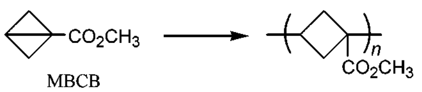
Introduction. Bicyclobutanes carrying electron-withdrawing substituents at the 1- and/or 3-positions are a remarkable class of reactive monomers. Either free radical or anionic polymerization occurs readily across the B-like 1,3-bond to give high molecular weight polymers consisting of 1,3-linked cyclobutane rings.[1] Such polymers have interesting properties including high glass transition temperatures, chemical and thermal stability, superior optical clarity, and resistance to depolymerization.

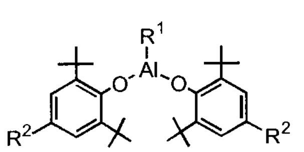
1,3-Disubstituted cyclobutanes exist as either cis or trans isomers. Accordingly the stereochemistry of the polybicyclobutanes becomes of interest, particularly for its influence on physical properties. Free radical polymerization of dimethyl bicyclobutane-1,3-dicarboxylate gave 95% trans linkages.[2] Similar polymerizations of various 1-monoesters gave polymers with trans/cis ratios of about 2/1.[3]

Anionic polymerization offers potentially better control of stereochemistry of polymers, but early attempts with *n*-butyllithium as initiator gave only low molecular weight products. In this Communication, we report the anionic polymerization of methyl bicyclobutane-1-carboxylate (MBCB) with combined initiators, *tert*-butyllithium (*t*-BuLi)/bis(2,6-di-*tert*-butylphenoxy)alkylaluminums, which are effective for stereospecific living polymerization of methacrylates[4−12] and acrylates.[13]



MBCB

Experimental Section. MBCB[14] and alkylaluminum bisphenoxides **1**−**5**[6,15] were prepared according to



(**1**) $R^1=CH_3$, $R^2=H$
(**2**) $R^1=C_2H_5$, $R^2=H$
(**3**) $R^1=C_2H_5$, $R^2=CH_3$
(**4**) $R^1=C_2H_5$, $R^2=Br$
(**5**) $R^1=i\text{-}C_4H_9$, $R^2=H$

the procedures reported previously. The anionic polymerizations were carried out in glass ampules filled with nitrogen, which were dried by passing it through molecular sieves 4A cooled at −78 °C. To aluminum bisphenoxide (0.21 mmol) in toluene (1 mL) was added a heptane solution of *t*-BuLi (0.07 mmol) at the polymerization temperature, and the reaction was initiated by adding MBCB (2 mmol). The reaction was terminated after 24 h by adding methanol containing HCl. The reaction mixture was concentrated to dryness under reduced pressure, and the residue was dissolved in chloroform. Insoluble inorganic materials were extracted with water, and the polymeric product was recovered by evaporating the chloroform under vacuum. ^{13}C NMR spectra were recorded in chloroform-*d* on a Varian Unity Inova 500 spectrometer operated at 125 MHz. Trans contents of the polymers were determined from the quaternary carbon NMR signals.[3,16] Molecular weights and molecular weight distributions were determined by size exclusion chromatography (SEC) using a JASCO 880-PU chromatograph equipped with Shodex SEC columns [KF-806L (30 cm × 0.8 cm) × 2] using chloroform as an eluent, and calibrated against standard PMMA samples (Shodex).

Results and Discussion. Anionic polymerization of MBCB was attempted in toluene by using several anionic initiators (Table 1). *t*-BuMgBr, known to initiate isotactic-specific living polymerization of methyl methacrylate,[17] did not give polymers at −78 °C (run 2) and neither did the more basic initiator *t*-BuLi (run 3). In contrast, when *t*-BuLi was used in combination with bis(2,6-di-*tert*-butylphenoxy)methylaluminum (**1**), the polymerization in toluene at −78 °C proceeded smoothly to give a polymer quantitatively (run 5). The use of *n*-Bu_3Al in place of **1** was not effective (run 4). These results suggest that the bulkiness of **1** is essential for the successful polymerization. As in the polymerization of methacrylates, **1** presumably coordinates with the propagating anions to prevent possible side reactions and with MBCB to protect the carbonyl group from the attack of *t*-BuLi.

Figure 1 shows ^{13}C NMR spectrum of poly(MBCB) prepared with *t*-BuLi/**1** (run 5), and of poly(MBCB) obtained with AIBN (run 1). The cyclobutane rings in the polymer backbone can be either cis or trans, and every carbon resonance therefore shows splitting owing to the cis−trans isomerism. The trans contents were determined from the split signals due to the quaternary carbons (trans, 44.3 ppm; cis, 46.4 ppm). The trans content of poly(MBCB) obtained with AIBN was 65.8%, in agreement with the previous report.[3] For the polymer prepared with *t*-BuLi/**1**, the trans content increased to 73.2%.

The structure of the aluminum bisphenoxides strongly affects the stereospecificity in the anionic polymerizations of methacrylate[4−12] and acrylate.[13] To examine such effects, MBCB was polymerized in toluene with *t*-BuLi in the presence of several aluminum compounds, as shown in Table 1. Changing the alkyl group attached to aluminum atom from methyl (**1**) to ethyl (**2**) drastically increased the trans content of the polymer from 73.2 (run 5) to 92.3% (run 7). A similar drastic change in stereospecificity is reported for the anionic polymerization of alkyl methacrylate, in which *t*-BuLi/**1** gives heterotactic polymers while *t*-BuLi/**2** leads to syndiotactic ones.[8] Further increase in the bulkiness of the alkyl group from ethyl (**2**) to isobutyl (**5**) inhibited the polymerization (run 11).

The temperature dependence of the stereospecificity of the polymerization was examined by using *t*-BuLi/**2** as an initiator. Lowering the polymerization tempera-

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† Osaka University.
‡ University of Arizona.

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Table 1. Polymerization of MBCB in Toluene for 24 h[a]

							solubility[d]	
run	initiator	temp/°C	yield/%	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	trans[c]/%	toluene	acetone
1	AIBN	60	100	39 600	2.84	65.8	○	○
2	*t*-BuMgBr	−78	0					
3	*t*-BuLi	−78	0					
4	*t*-BuLi/*n*-Bu$_3$Al[e]	−78	0					
5	*t*-BuLi/**1**[e]	−78	96	13 500	2.90	73.2	○	○
6	*t*-BuLi/**2**[e]	−95	98	17 700	1.85	88.1	×	×
7	*t*-BuLi/**2**[e]	−78	98	27 200	2.50	92.3	×	×
8	*t*-BuLi/**2**[e]	0	100	11 100	3.04	82.2	△	×
9	*t*-BuLi/**3**[e]	−78	100	11 000	3.17	89.7	×	×
10	*t*-BuLi/**4**[e]	−78	100	39 000	1.31	86.3	×	×
11	*t*-BuLi/**5**[e]	−78	0					
12	**2**[e]	−78	0					

[a] Monomer 2 mmol, initiator 0.07 mmol, and toluene 1 mL. [b] Determined by SEC using chloroform as an eluent with calibration using standard PMMA samples. [c] Determined from split ^{13}C NMR signals of quaternary carbons. [d] Solubility was examined at a concentration of 10 mg/mL: (○) soluble; (△) partially soluble; (×) insoluble. All the polymers were soluble in chloroform. [e] Aluminum compound 0.21 mmol.

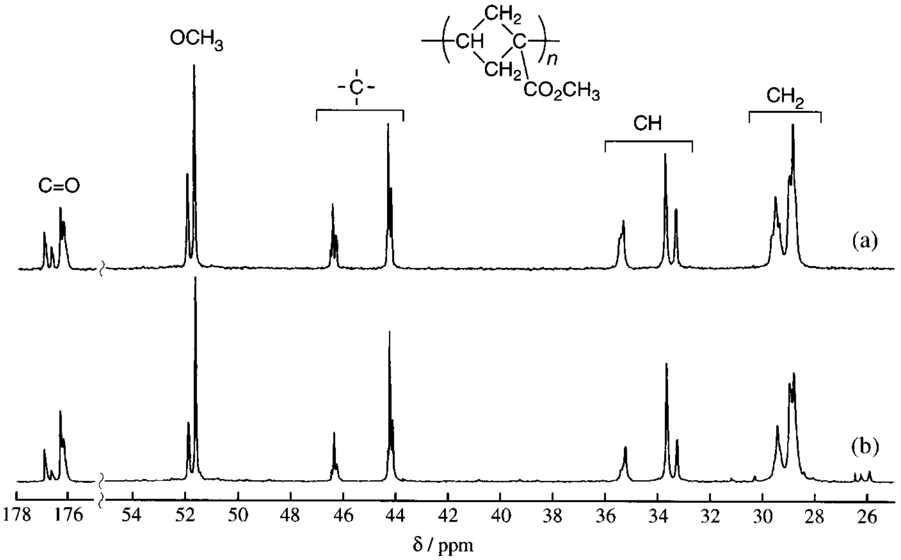


Figure 1. 125 MHz ^{13}C NMR spectra of poly(MBCB)s prepared with AIBN at 60 °C (a) and with *t*-BuLi/**1** at −78 °C (b), measured in chloroform-*d* at 55 °C.

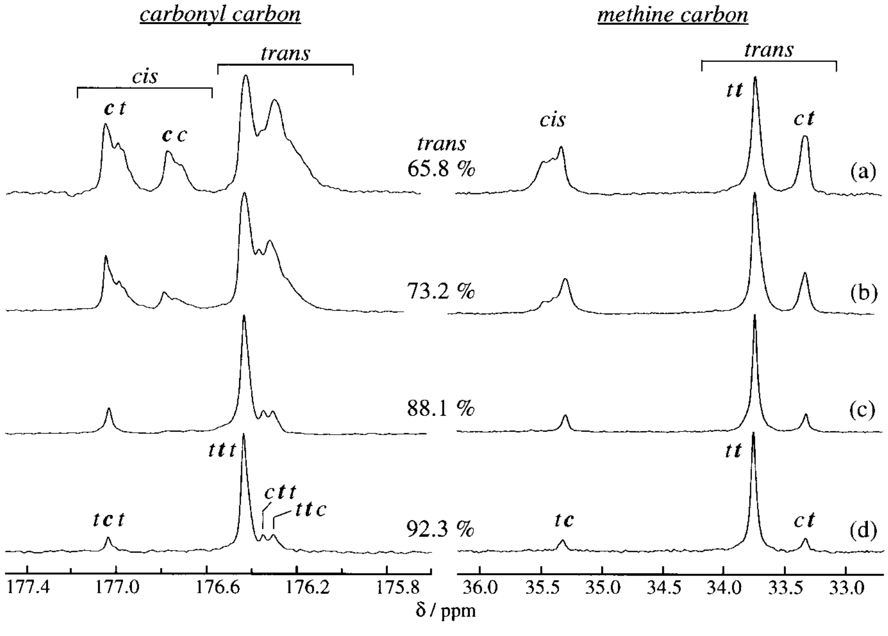


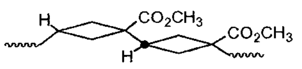
Figure 2. 125 MHz ^{13}C NMR spectra of methine and carbonyl carbons of poly(MBCB)s prepared with AIBN at 60 °C (a), *t*-BuLi/**1** at −78 °C (b), *t*-BuLi/**2** at −95 °C (c), and *t*-BuLi/**2** at −78 °C (d), measured in chloroform-*d* at 55 °C.

ture from −78 to −95 °C did not contribute to enhancement of trans content (run 6; trans 88.1%). The polymerization at 0 °C produced a polymer with lower regularity (run 8; trans 82.2%).

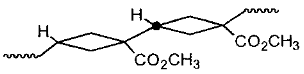
Introducing a substituent at para positions of the phenoxy groups changes the Lewis acidity of the aluminum bisphenoxides. To investigate the effect of Lewis acidity of the aluminum compounds on the polymerization, MBCB was polymerized in toluene at −78 °C with *t*-BuLi in combination with **3** (run 9) or **4** (run 10): the former has an electron-donating methyl group at the para position and may have decreased Lewis acidity, and the latter has an electron-withdrawing bromine atom increasing the acidity. Both co-initiators lowered the trans contents of the polymers, indicating that the aluminum bisphenoxide **2**, having a medium acidity, gives the best control of stereospecificity of the polymerization.

The solubility of poly(MBCB)s was found to depend on their trans contents. While all the poly(MBCB)s shown in Table 1 were soluble in chloroform, the poly(MBCB)s with higher trans contents were insoluble in toluene and acetone. It is thus evident that the stereocontrol of poly(MBCB) is essential for its property control.

Figure 2 shows carbonyl and methine carbon resonances of poly(MBCB)s with different trans contents. Both signals split into two principal groups of peaks, reflecting cis−trans isomerism within the cyclobutane ring units in the main chain. The further splitting of each group (cis or trans) is due to the stereochemical sequences. The methine carbon signals of the trans unit clearly split into two peaks (33.3 and 33.7 ppm), which may be assigned to cis-trans (*ct*) and trans-trans (*tt*) sequences, respectively:

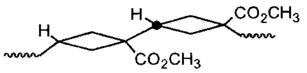


cis-trans (*ct*)



trans-trans (*tt*)

The cis−trans structure of the other neighboring cyclobutane unit (the unit attached to the 3-carbon) apparently has much less influence. The methine signal of the cis units is a little more complicated, but becomes simpler as the trans content increases. The small signal observed for the poly(MBCB)s with high trans contents can be assigned to trans−cis (*tc*) sequence:



trans-cis (*tc*)

The carbonyl carbon signals actually show triad splittings for both trans and cis units: for the trans unit, *ttt*, *ttc*, *ctt* and *ctc*, and for the cis unit, *tct*, *tcc*, *cct* and *ccc*. The observed peaks are due to overlap of these four peaks. The assignments shown in Figure 2 were made based on the relative peak intensity and calculated fractions of these triad sequences by assuming Bernoullian statistics as the first approximation. The results suggest that long trans sequences in the polymer are responsible for the unusual solubility of stereoregular poly(MBCB)s. The detailed structural analysis will be reported in a future publication.

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