

The Dual-Site Alternating Cyclocopolymerization of 1,3-Butadiene with Ethylene

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Supporting Information

Experimental:

Catalysts

The catalysts **1**, **2** and **3** were provided by Dr Wendy Fan and synthesized according to literature as listed in an earlier publication.¹

Materials

All manipulations involving air and moisture sensitive compounds were carried out under dry nitrogen atmosphere using standard glove box and Schlenk techniques. Ethylene (Matheson, polymerization grade) was purified by passing through columns of Alltech Oxy-trap and Alltech gas drier. 1,3-Butadiene (99%, Aldrich) was used by vapor transfer directly into the polymerization vessel. Methylaluminoxane (MAO), type 3A, purchased from Akzo Nobel, was dried in vacuo prior to use. Toluene (Aldrich) was purified by passing through a tower of alumina and Q5 copper catalyst.






Polymerizations

Copolymerizations were carried out in a 250 ml glass autoclave equipped with a magnetic stirrer. The reactor was filled with a 25-30 ml mixture of toluene and 200 mg of MAO and sealed under nitrogen atmosphere. The desired amount of 1,3-butadiene was then transferred into the reactor. The reactor was brought to 25°C in a water bath. The reaction mixture was then saturated with ethylene by applying a constant overpressure for 30 min. Metallocene solution (3-8 ml) was injected under ethylene and copolymerization was carried out for 2 to 24 hours. Ethylene pressure is kept constant during polymerization, and the copolymerizations were quenched by injecting methanol and venting off excess ethylene. The copolymers were precipitated by pouring into methanol (100 ml) acidified with conc. HCl (0.5 ml) for 5 mins, and then isolated and stirred in methanol and stirred overnight. All polymers were dried under vacuum to constant weight.

Characterization

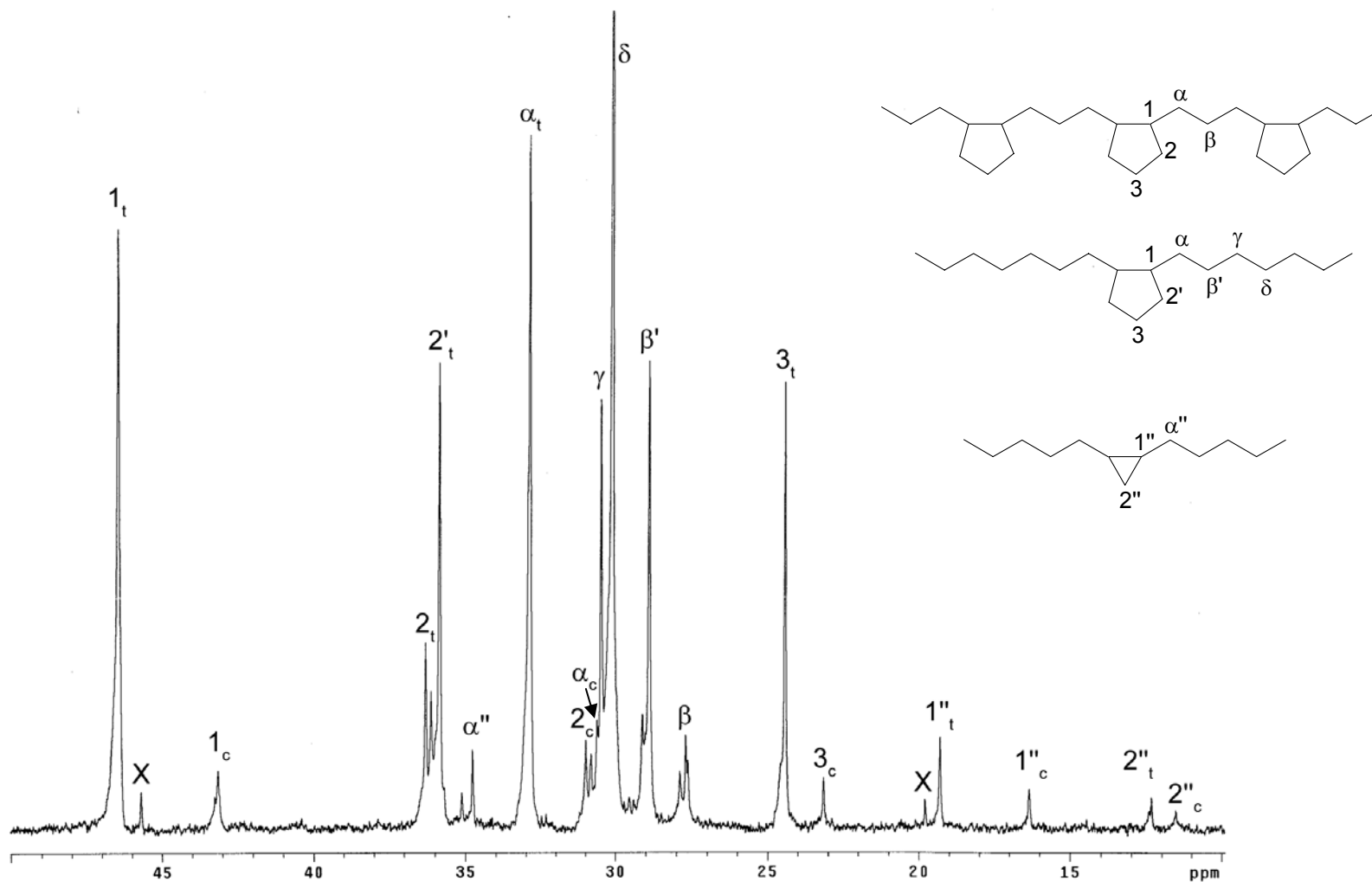
¹³C NMR spectra of the polymers were recorded at 80°C, using tetrachloroethane/d₂- tetrachloroethane (4:1, v/v) as solvent, on a Varian Inova 300 spectrometer operating at 75.4 MHz. The peak assignments of the ¹³C NMR spectra of the copolymers were made by comparing the spectra of copolymers with various 1,3-BD contents and also with the ¹³C NMR assignment reported in literature.

Table S1. Molecular Weight Analysis of Selected Ethylene/1,3-Butadiene Copolymers

Run No.	Metal-locene	P _E (psig)	BD in feed (mmol)	[Zr] (μM)	[Al]/[Zr]	Time (hr)	yield (g)	activity (kg/mol·Zr·hr)	BD in polym. (mol%)						M _n	M _w	M _n /M _w	T _g (°C)	T _m (°C)
										(%) ^a	(%) ^a	(%) ^a	(%) ^a	trans (%) ^b					
1b	1	8	93	438	240	1.25	1.34	74	12	14	trace	4	82	83	21600	210000	9.7	-35.5	-30.4 to 56.5 (25.2) ^d
1d	1	30	35	52	1900	0.25	0.11	240	trace	trace	0	0	>99	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	-	21.9 to 122.8 (109.0) ^d
2a	2	5	98	92	910	22	0.22	3	32	46	0	0	54	91	21300	40200	1.9	n.d. ^c	n.d. ^c
2b	2	8	90	150	570	5	0.33	11	31	44	0	0	56	91	10000	109700	11.0	-7.6	-
2c	2	15	93	150	570	6	0.52	15	30	43	0	0	57	90	20600	82300	4.0	-10.6	-
2d	2	30	35	107	920	2.25	0.33	39	22	28	0	0	72	90	18400	42400	2.3	-25.7	-
3a	3	5	94	268	320	24	0.07	0.26	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c
3b	3	8	93	268	320	20	0.14	0.65	17	21	4	trace	75	90	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c
3d	3	30	35	184	540	3	0.25	13	5	5	1	0	93	87	33300	62400	1.7	-25.3	0 to 135.9 (90.1) ^d

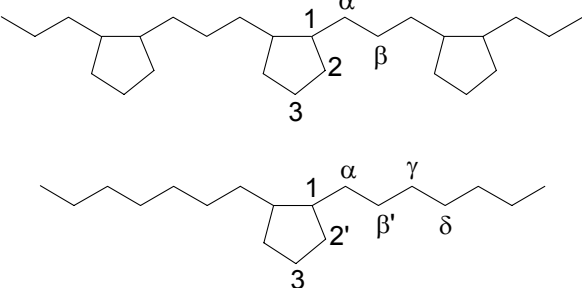
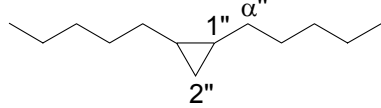
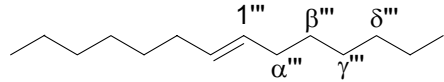
^a Relative abundances of various enchainment monomer units. ^b Mole fraction of cyclopentane rings *trans*. ^c Not determined. ^d Temperature at peak of melting exotherm.

Figure S1. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of an Ethylene/1,3-Butadiene Copolymer obtained with **3**/MAO (entry 3b, Table 1)



X : solvent impurities

Table S2. ^{13}C NMR Peak Assignment for E/BD Copolymers²

	Peak	Chem. Shift		Peak	Chem. Shift
	3 _c	23.2		2'' _c	11.6
	3 _t	24.5		2'' _t	12.4
	β	27.7		1'' _c	16.4
		27.9		1'' _t	19.3
	β'	28.9		α''	34.8
	δ	30.1		γ'''	29.6
	α _c , γ	30.5		δ'''	29.9
	2 _c	31.0		β'''	30.1
	α _t	32.9		α'''	32.9
	2' _t	35.9		1'''	130.8
	2 _t	36.1			
		36.3			
	1 _c	43.2			
	1 _t	46.5			

All chemical shifts are in ppm, and measured in d₂-tetrachloroethane/tetrachloroethane (1:10) and referenced to d₂-tetrachloroethane at 74.4 ppm.

Subscripts "c" and "t" denotes *cis* and *trans* stereoisomers of the cyclic structures.

References

- (1) (a) Chen, Y. X.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1995**, *497*, 1-9. (b) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998-1005.
- (2) (a) Galimberti, M.; Albizzati, E.; Abis, L.; Bacchilega, G. *Makromol. Chem.* **1991**, *192*, 2591-2601. (b) Llauro, M. F.; Monnet, C.; Barbotin, F.; Monteil, V.; Spitz, R.; Boisson, C. *Macromolecules* **2001**, *34*, 6304-6311. (c) Pragliola, S.; Milano, G.; Guerra, G.; Longo, P. *J. Am. Chem. Soc.* **2002**, *124*, 3502-3503.