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Rapid Quantitative ^{1}H-^{13}C Two-Dimensional NMR With High Precision

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1. General information about the content and triads calculation of poly(ethylene-*co*-1-hexene)

In this work, we are primarily concerned with substitutional isomerisims of the sequence type of poly(ethylene-*co*-1-hexene), which are the result of adding either an ethylene or 1-hexene monomer unit to the end of a growing polymer chain, whereas the previous monomer unit added is either ethylene or 1-hexene.[1-5] The common way to describe these sequences is by means of *n*-ads, namely monads (one monomer unit), diads (two monomer units), triads, etc. The sum of the mole fractions of the two monads in the poly(ethylene-*co*-1-hexene) system, ethylene (E) and 1-hexene (H) is unity, i.e., [E] + [H] =1. In the same way, six triads are possible (EEE, EEH, HEH, EHE, EHH, HHH), and the sum of their mole fractions is unity. It is easily seen that [EEE] + [EEH] + [HEH] = [E], and [HHH] + [EHH] + [EHE] = [H].[6] In addition, it is required that the necessary relationship [EEH] + 2[HEH] = [EHH] + 2[EHE] is maintained.

The chemical shift assignments of the ^{13}C NMR spectrum of poly(ethylene-*co*-1-hexene) were well reported in the literature, with essentially full agreement among independent reports. For the purpose of determining triads mole fractions, Hsieh and Randall introduced the concept of collective assignments with the ^{13}C NMR spectrum, in which the spectrum was divided into baseline-resolved regions and then integrated region by region,[7-8] as shown in **Table S2**. The integrated intensities of the various collective assignment regions (A-G) can be related algebraically, in many ways, to the content of the six different triads in EH copolymer. Considering that the long T_1 value of methyl carbons in the region H required long repetition delays, we choose the following equations for the determination of triads mole fractions: k [EHE] = B, k [EEH] = E, k [HEH] = F, k [EHH] = 2 (G −A − B), k [HHH] = 2A + B − G, k [EEE] = 0.5D − 0.5G − 0.25E. Notably, almost all the signals correlated with the equations are ascribed to CH_2 carbons, except the resonance in region B assignable to CH carbon. In addition, the ethylene/1-hexene copolymer used here are LLDPE (1-hexene incorporation ≤ 10 mol %) without HH sequences ($S_{\alpha\alpha}$), since no signal in region A are detected. The equation of k [EHE] = 0.5E + F then can be deduced from the expression [EEH] + 2[HEH] = [EHH] + 2[EHE]. Consequently, the factor of the degree of the substitution on the accuracy of triad mole fractions is almost to the same extent.

Reference:

1. F. A. Bovey, *High-Resolution NMR of Macromolecules*; Academic Press: NewYork, 1972.
2. F. A. Bovey, *Polymer Conformation and Configuration*; Academic Press:NY, 1969.
3. F. A. Bovey, *High-Resolution NMR of Macromolecules*; Academic Press: New York, 1979.
4. J. C. Randall, *Polymer Sequence Determination*; Academic Press: New York, 1977.
5. D. E.Axelson, G. C.Levy, L. Mandelkern, *Macromolecules* 1979, **12**, 41−52.
6. J. C. Randall, *J Macromol. Sci., Rev. Macromol. Chem. Phys.* 1989, **C**29, 201−317.
7. E. T.Hsieh, J. C. Randall, *Macromolecules* 1982,**15**, 1402−1406.
8. H. Merkle, H. Wei, M. Garwood, K. Uğurbil, *J. Magn. Reson.* 1992, **99**, 480−494.

Table S1 Composition and monomer sequence distributions of the two model EH samples calculated by quantitative ^{13}C NMR.

Sample ID	NMR method	Time(min)	Mole fraction (%)		Monomer sequence distributions		
			ethylene	1-hexene	EEE	EEH+HEE	EHE
EH-1	^{13}C NMR	1390	91.40	8.60	74.20	17.20	8.60
EH-2	^{13}C NMR	1140	95.92	4.08	87.76	8.16	4.08

Table S2 ^{13}C chemical shift assignments for the poly(ethylene-*co*-1-hexene), as determined by Hsieh and Randall

region	^{13}C chemical shift range (ppm)	Carbon types	Contributing n-ads
A	39.5-42.0	CH_2 (αα)	HHHH, HHHE, EHHE
B	38.0	CH (EHE)	EHE
C	35.64	CH (EHH)	EHH
	34.7-34.9	CH_2 (αγ)	EEH,EHE, HEH
	34.40	CH_2(αδ+)	EHEE
	34.00	CH_2 ($4B_4$)	EEH, HEH, EHE, HHE
D	30.79	CH_2 (γγ)	HEEH
	30.33	CH_2 (γδ+)	EEEH
	29.84	CH_2 (δδ)	EEEE
	29.40	CH_2 ($3B_4$)	EHE
	29.21	CH_2 ($3B_4$)	HEH
E	27.0-27.16	CH_2 (βδ+)	EEH, EHE
F	24.40	CH_2 (ββ)	EHE, HEH
G	23.26	CH_2 ($2B_4$)	EEH, HEH, EHE, HHE
H	14.12	CH_3 ($1B_4$)	EEH, HEH, EHE, HHE

Table S3. Repeatability of 2D HSQC with NUS for Sample EH-1 and EH-2.

Sample		EH-1					EH-2				
method	evaluation	triads			content		triads			content	
		EEE	EEH	EHE	E	H	EEE	EEH	EHE	E	H
HSQC/NUS 25%	mean	0.880	0.080	0.040	0.960	0.040	0.748	0.168	0.084	0.916	0.084
	SD	0.005	0.005	0.005	0.005	0.005	0.005	0.006	0.006	0.005	0.006
	CV%	0.57	6.25	12.5	0.63	12.5	0.67	3.57	7.14	0.55	7.14
HSQC/NUS 35%	mean	0.877	0.082	0.041	0.959	0.041	0.742	0.172	0.086	0.914	0.086
	SD	0.003	0.003	0.003	0.003	0.003	0.003	0.004	0.004	0.004	0.004
	CV%	0.34	3.66	7.32	0.31	7.32	0.40	2.33	4.65	0.44	4.65
HSQC/NUS 50%	mean	0.877	0.082	0.041	0.959	0.041	0.745	0.170	0.085	0.915	0.085
	SD	0.002	0.002	0.002	0.002	0.003	0.001	0.002	0.002	0.002	0.002
	CV%	0.22	2.42	4.86	0.20	4.86	0.14	1.18	2.36	0.22	2.36
HSQC/NUS 75%	mean	0.874	0.084	0.042	0.958	0.042	0.742	0.172	0.086	0.914	0.086
	SD	0.002	0.003	0.003	0.002	0.003	0.002	0.003	0.003	0.002	0.003

	CV%	0.22	3.50	7.00	0.20	7.00	0.27	1.74	3.48	0.22	3.48

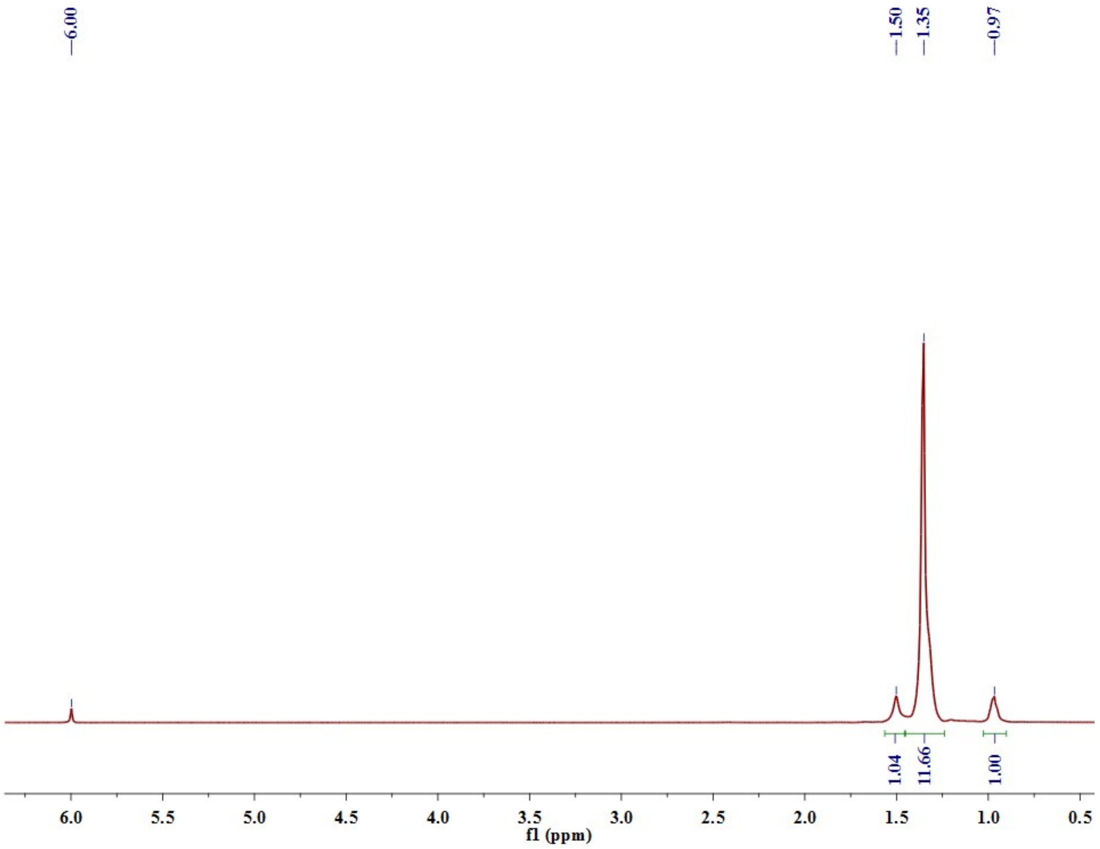

Fig. S1. Liquid-state ^{1}H NMR spectrum (400.13 MHz) of EH-1 sample dissolved in 1, 1, 2, 2-tetrachloroethane-d$_4$ at 120°C with D$_1$= 10 s and NS = 64.

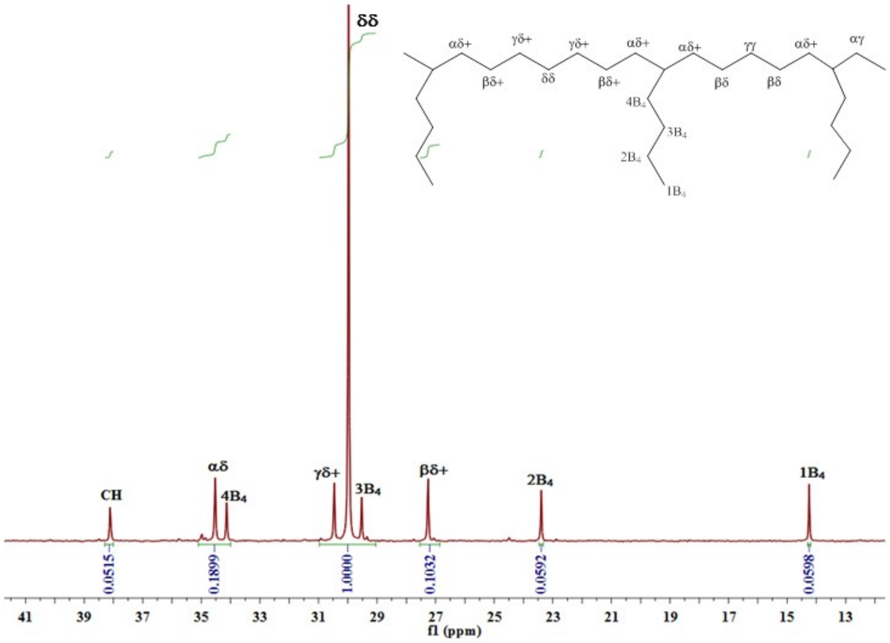

Fig. S2. Liquid-state ^{1}H NMR spectrum (a, 400.13 MHz) and ^{13}C NMR spectrum (b, 100.19 MHz) of EH-1 sample dissolved in 1, 1, 2, 2-tetrachloroethane-d$_4$ at 120°C (with WALTZ-16 decoupling) with D$_1$= 42 s and NS =1900.

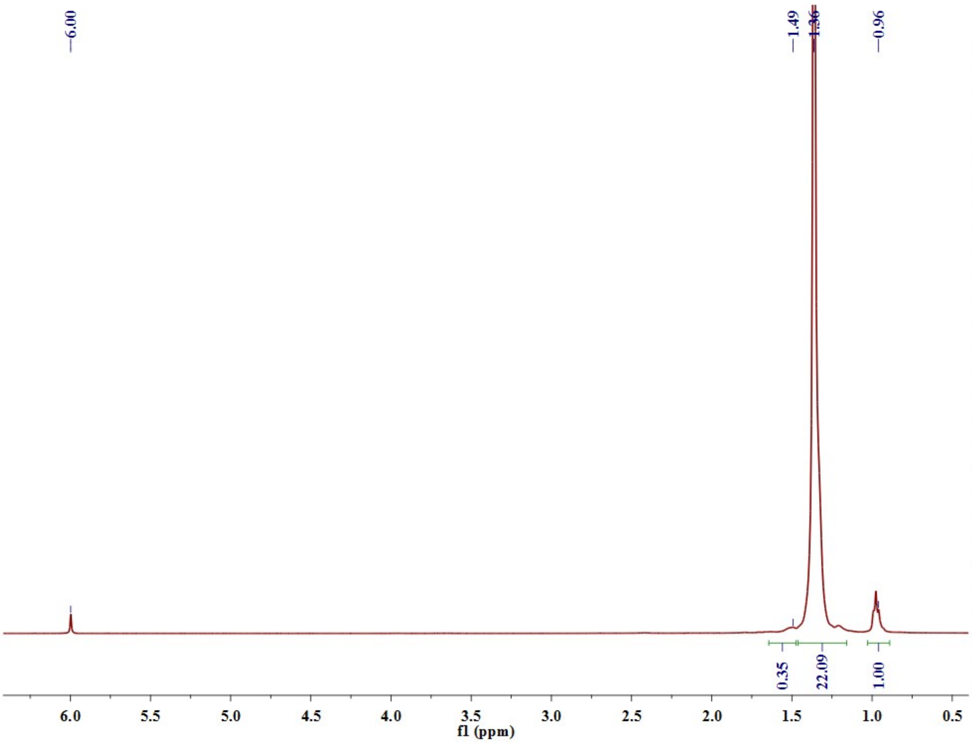

Fig. S3. Liquid-state ^{1}H NMR spectrum (400.13 MHz) of EH-2 sample dissolved in 1, 1, 2, 2-tetrachloroethane-d_4 at 120°C with D_1= 10 s and NS = 64.

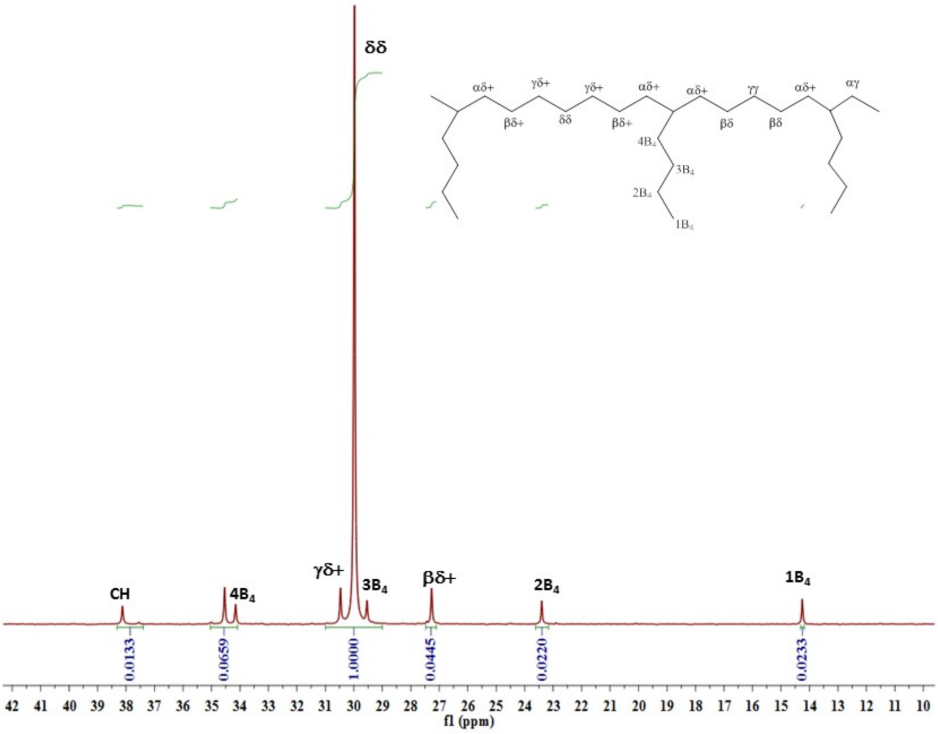

Fig. S4. Liquid-state ^{13}C NMR spectrum (101MHz) of EH-2 sample dissolved in 1, 1, 2, 2-tetrachloroethane-d_4 at 120°C (with WALTZ-16 decoupling) with D_1= 42 s and NS =1500.

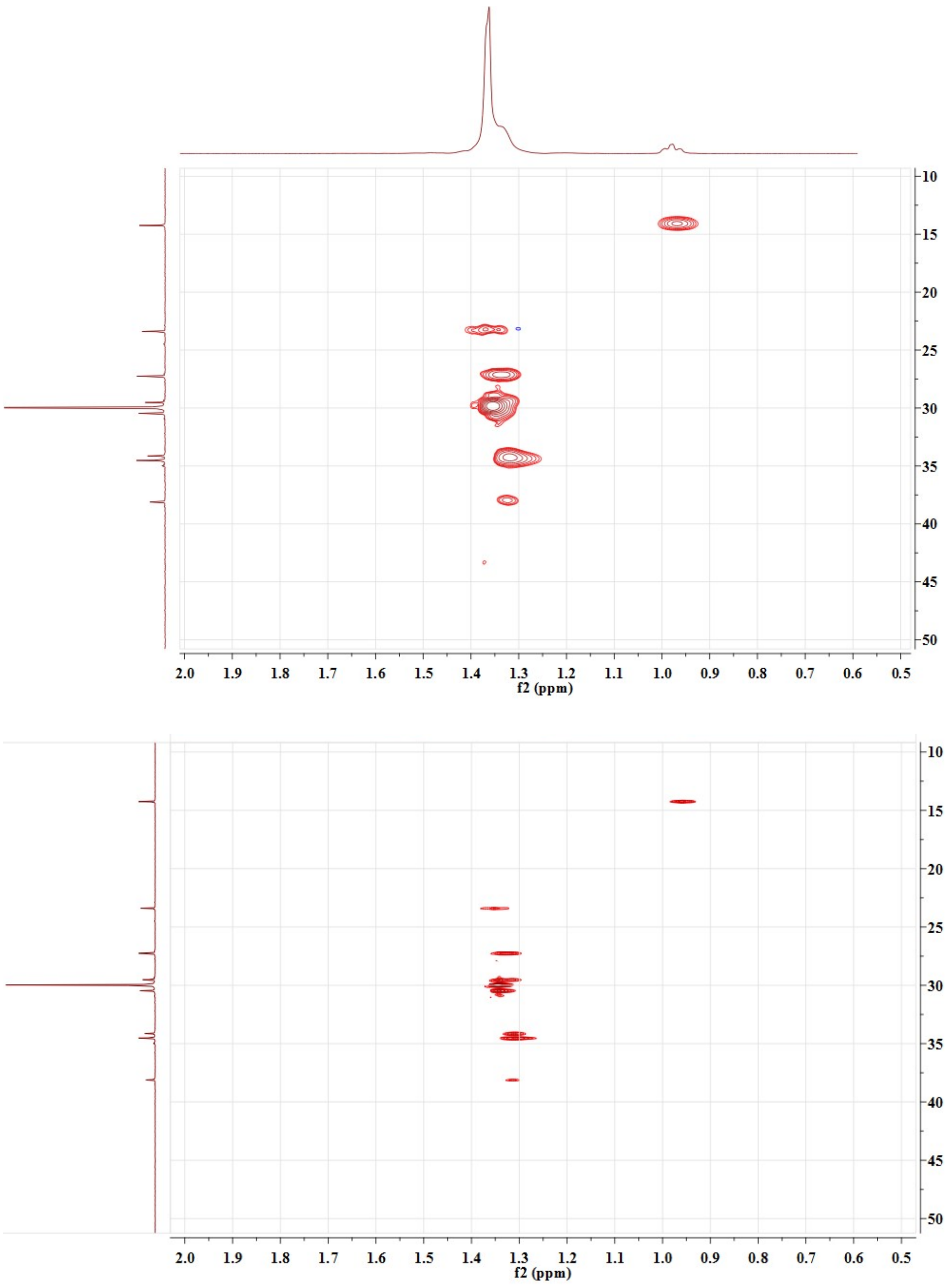

Fig. S5. Comparison of 2D HSQC spectra of EH-2 sample recorded on 400MHZ Bruker spectrometer, with TD = 128 (top) and TD = 512 (bottom) in F_1, respectively.