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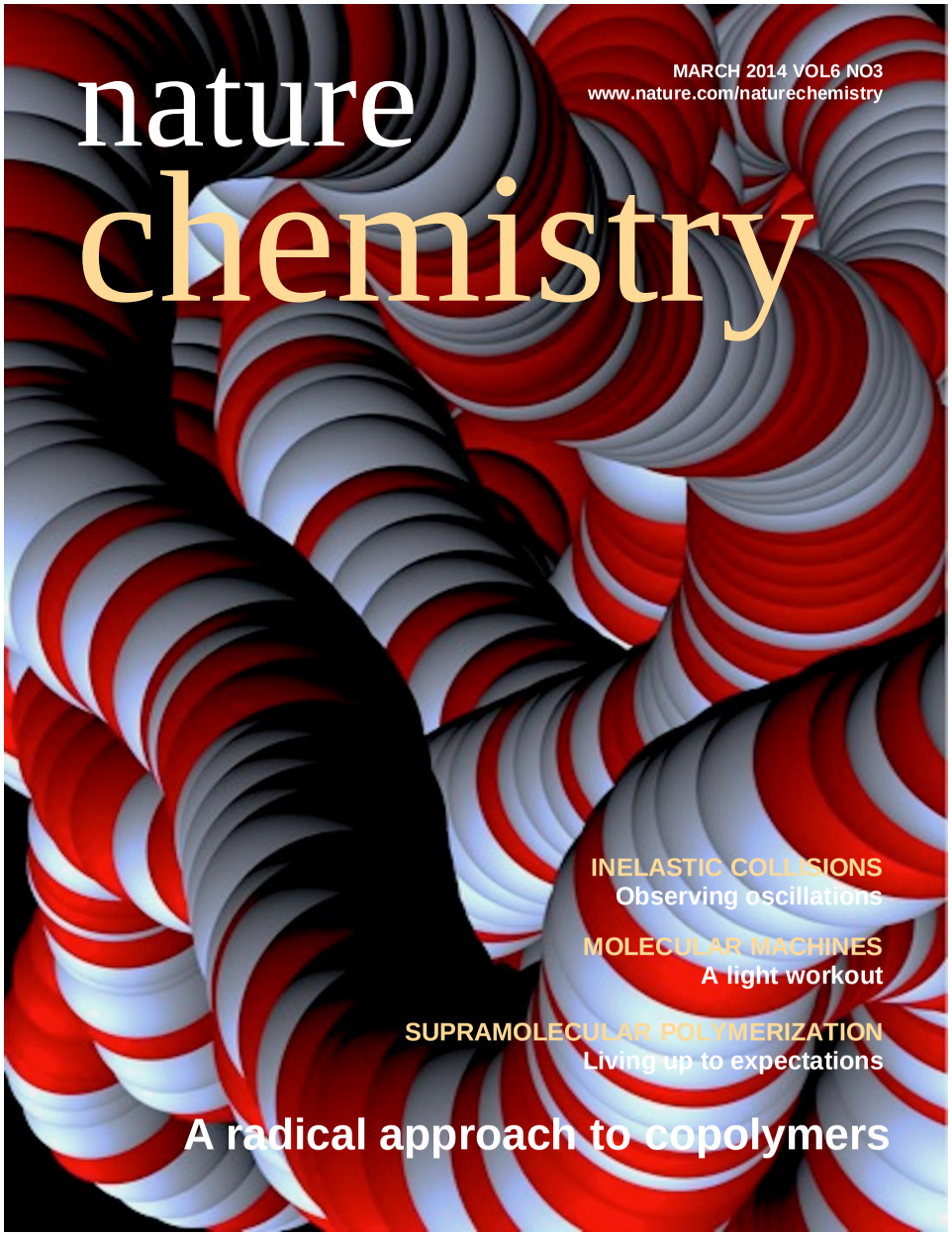

nature chemistry
ARTICLES
PUBLISHED ONLINE: 26 JANUARY 2014 | DOI: 10.1038/NCHEM.1850

Precision design of ethylene- and polar-monomer-based copolymers by organometallic-mediated radical polymerization

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The copolymerization of ethylene with polar monomers is a major challenge when it comes to the manufacture of materials with potential for a wide range of commercial applications. In the chemical industry, free-radical polymerization is used to make a large proportion of such copolymers, but the forcing conditions result in a lack of fine control over the architecture of the products. Herein we introduce a synthetic tool, effective under mild experimental conditions, for the precision design of unprecedented ethylene- and polar-monomer-based copolymers. We demonstrate how an organocobalt species can control the growth of the copolymer chains, their composition and the monomer distribution throughout the chain. By fine tuning the ethylene pressure during polymerization and by exploiting a unique reactive mode of the end of the organometallic chain, novel block-like copolymer structures can be prepared. This highly versatile synthetic platform provides access to a diverse range of polymer materials.

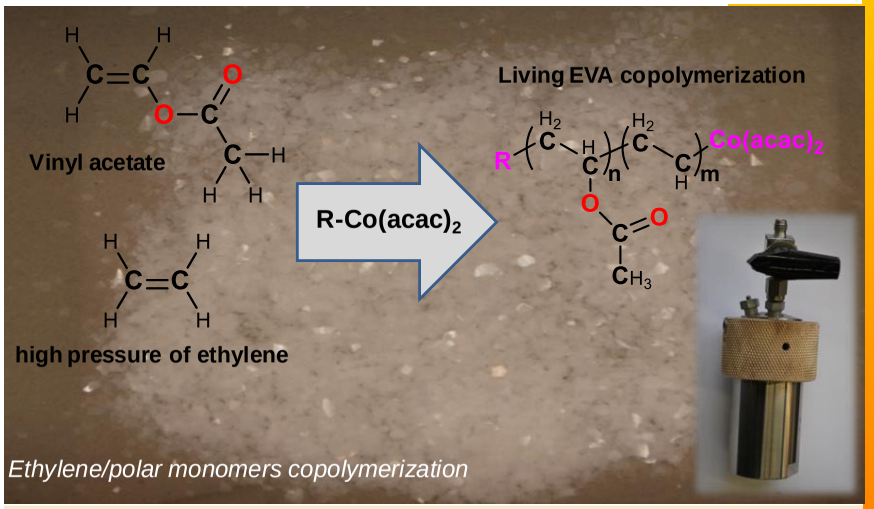

Table 1 | Statistical organometallic-mediated radical copolymerization of ethylene and polar comonomers (M).

Entry	M	Pressure (bar)	Comonomer conversion (%)*	M_n (g mol^{-1})	M_w/M_n	Composition*		T_g (°C)†
						F_M	$F_{ethylene}$	
1	VAc	10	99	8,800‡	1.23‡	0.87 (0.85)‖	0.13 (0.15)‖	26.2
	VAc	25	80	11,200‡	1.37‡	0.67	0.33	7.4
	VAc	50	55	8,900‡	1.34‡	0.46 (0.49)‖	0.54 (0.51)‖	−7.7
2	NMVA	10	85	9,100§	1.18§	0.82 (0.80)‖	0.18 (0.20)‖	124.8
	NMVA	50	66	4,700§	1.09§	0.50 (0.46)‖	0.50 (0.54)‖	81.7
3	AN	10	95	23,700§	1.23§	0.95 (0.93)‖	0.05 (0.07)‖	-
	AN	50	95	24,900§	1.31§	0.87 (0.83)‖	0.13 (0.17)‖	-

Conditions: 40 °C, 24 hours, R-Co = 4.0 × 10^{-4} mol, M/R-Co = 100, magnetic stirring at 500 r.p.m. *Determined by ^{1}H NMR spectroscopy. †Determined by DSC analysis. ‡Determined by SEC in THF using PS calibration. §Determined by SEC in DMF containing 0.025 M LiBr using a multiangle light-scattering detector. ‖Determined by elemental analysis from O or N concentrations. THF, tetrahydrofuran; PS, polystyrene; DMF, dimethylformamide.