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Long-Spaced Polyketones from ADMET Copolymerizations as Ideal Models for Ethylene/CO Copolymers

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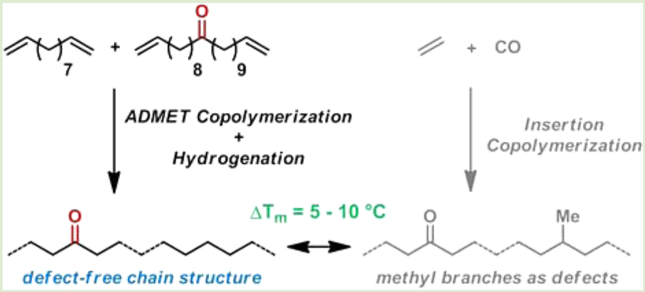
Supporting Information



ABSTRACT: Long-spaced polyketones containing 0−52.6 ketone groups per 1000 methylene units were prepared by ADMET copolymerization of docosa-1,21-dien-11-one (**1**) with undeca-1,10-diene (**2**), followed by exhaustive hydrogenation. Melting point differences of 5−10 °C were found between these polyketones and their reported congeners from ethylene/CO copolymerizations with comparable CO contents, which were related to additional methyl branching occurring in insertion copolymerization. Consequently, ADMET-derived polyketones can act as defect-free model polyketones. Comparison with polymers containing the same degrees of other carbonyl functionalities (esters, carbonates) shows that the partial compensation of the disturbance of polyethylene crystallization goes along with the groups' polarity.

Copolymers from ethylene and polar monomers are of general interest since physical and chemical materials properties (like melting temperature, crystallinity, printability, adhesion, photo degradability) are significantly influenced already by low degrees of polar group functionalization.[1] Copolymerization of ethylene and carbon monoxide (CO) yields aliphatic polyketones, and different preparative approaches have been developed over the last decades. From free-radical copolymerization at high pressures, copolymers with various CO incorporation rates were obtained, containing also significant degrees of branching.[2] For example, such copolymers with about 1 mol % CO can be applied as photodegradable low-density polyethylene (LDPE) analogues.[3] In general, CO is an attractive comonomer as it can be obtained from virtually any carbon feedstock at low cost.

Insertion copolymerization usually yields an alternating copolymer, that is a γ-polyketone. Cationic Pd(II) diphosphine catalysts were found to be particularly suited.[4] However, γ-polyketones suffer from their limited processability due to their high melting temperatures (>250 °C), where polymer degradation already becomes relevant, and their insolubility in most common solvents. A first example for nonalternating ethylene/CO insertion copolymerization was reported by Drent and co-workers, generating polyketones with lower CO contents using a Pd(II) precursor with a phosphine-sulfonate ligand.[5] Subsequently, further ethylene/CO copolymers with desirably lower CO contents were prepared (typically with molecular weights between 10^3 and 10^4 g mol^{-1}) and intermediate to strictly alternating γ-polyketone and polyethylene.[6−10] Müller and co-workers reported melting points between 121 and 128 °C for copolymers with CO incorporations between 0 and 5.5 mol % (0−29.1 ketone groups per 1000 CH_2 units), which however contain also relevant amounts of methyl branches (between 2 and 8 branches per 1000 CH_2 units).[11] During insertion (co)-polymerization, methyl branching arises from β-hydride elimination, followed by a 2,1-reinsertion of the resulting olefin into the catalytically active species. Since methyl branches disturb crystallization of hydrocarbon polymer chains and affect the melting temperature, it remains unclear if the melting point depression of the reported polyketones compared to linear polyethylene (T_m = 134 °C)[12] is mainly related to methyl or ketone groups. To overcome this issue, defect-free polyketones are desirable.

An established approach for the preparation of functionalized or branched model polyethylenes is acyclic diene metathesis (ADMET) copolymerization of appropriately functionalized or branched α,ω-dienes with nonfunctionalized α,ω-dienes. Here, the formation of additional undesired alkyl branches is excluded from the olefin metathesis mechanism. Postpolymerization hydrogenation of the resulting unsaturated copolymers yields saturated compounds. Wagener and co-workers reported the preparation of methyl and butyl branched polyethylenes with various branching contents as models for ethylene/propylene and ethylene/1-hexene copolymers,[13,14] while different carbonyl functionalized polyethylenes (polyamides,[15] polyesters,[16] and polycarbonates[17]) were prepared by us, bridging the gaps between long-chain polycondensates prepared from traditional polycondensation methods and linear polyethylene.

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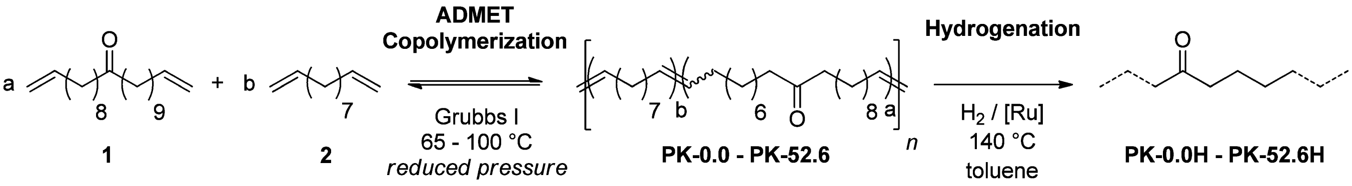
Scheme 1. Preparation of Long-Spaced Polyketones by ADMET Copolymerization and Post-Polymerization Hydrogenation[a]



[a] The designation "**PK-*X***" indicates the number (X) of ketone groups per 1000 methylene units derived from the initial monomer ratios applied for copolymerizations. The additional "H" indicates hydrogenated, saturated polyketones "**PK-*X*H**". Note that in the case of consecutive incorporation of the functionalized monomer **1**, 18, 19, or 20 aliphatic carbon atoms separate the ketone groups, depending on the orientation of the nonsymmetric diene.

Table 1. Compositions, Molecular Weights, and Melting Properties of Long-Spaced Polyketones

compound	monomer **1** (mol %)	theor. ketone groups per 1000 CH_2 units[a]	found ketone groups per 1000 CH_2 units[b]	M_n (g mol^{-1}) / M_w/M_n (GPC)[c]	M_n (g mol^{-1}) / M_w/M_n (GPC)[d]	M_n (g mol^{-1}, NMR)[e]	T_m[f] (°C) before / after hydrogenation	ΔH[f] (J g^{-1}) before / after hydrogenation
PK-52.6(H)	100.0	52.6	51.6	12900 / 3.4	3800 / 3.4	4600	95 / 125	107 / 176
PK-44.2(H)	71.4	44.2	43.4	14800 / 2.3	3800 / 3.2	5000	86 / 126	129 / 192
PK-40.1(H)	60.2	40.1	39.5	15100 / 1.7	3200 / 2.7	6600	85 / 125	125 / 240
PK-29.1(H)	36.9	29.1	30.7	11000 / 2.5	3800 / 3.9	9100	68 / 125	110 / 196
PK-19.9(H)	22.4	19.9	18.4	12900 / 2.0	4500 / 2.7	5600	59 / 128	121 / 225
PK-10.0(H)	10.0	10.0	11.1	23800 / 2.1	4700 / 2.5	7600	53 / 131	114 / 251
PK-5.4(H)	5.1	5.4	5.5	21700 / 1.8	6300 / 3.1	11600	49 / 131	108 / 243
PK-1.1(H)	1.0	1.1	1.2	11200 / 1.9	5000 / 2.1	7000	43 / 132	115 / 257
PK-0.0(H)	0.0	0.0	0.0	16600 / 2.3	10000 / 2.4	9200	42 / 134	117 / 276

[a] Calculated from the monomer weight ratios applied. [b] Determined by ^1H NMR spectroscopy of the unsaturated polyketones. [c] Determined on the unsaturated polyketones by GPC in THF at 40 °C vs polystyrene standards. Note that this method typically overestimates molecular weights of linear hydrocarbon polymers. [d] Determined on the saturated polyketones by GPC in 1,2,4-trichlorobenzene at 160 °C vs polyethylene standards. [e] Determined by end group analysis from ^1H NMR spectroscopy (of saturated polyketones). [f] From DSC at a heating/cooling rate of 10 °C min^{-1}. Peak T_m determined from the second heating cycle.

As an example for a defect-free aliphatic polyketone, Watson and Wagener reported ADMET homopolymerization of a symmetric ketone functionalized diene, followed by hydrogenation of the olefinic double bonds.[18] The resulting polymer contains ketone groups on every 19th backbone carbon atom (55.6 ketone groups per 1000 CH_2 units), which corresponds to a precisely functionalized ethylene/CO copolymer with 10.0 mol % CO incorporation and displays a melting point of 134 °C, providing beneficial insights into the crystalline properties of these functional polyolefins. However, perfectly regularly spaced polyketones can hardly act as satisfying models for random ethylene/CO copolymers.

In order to access the relevant regime of lower ketone group contents and also to achieve a nonregular microstructure, we used docosa-1,21-dien-11-one (**1**) as a nonsymmetric ketone functionalized α,ω-diene together with undeca-1,10-diene (**2**) as a nonfunctionalized α,ω-diene in ADMET copolymerizations (Scheme 1; for preparative details, see Supporting Information). Different monomer ratios were copolymerized applying 0.5 mol % Grubbs first generation catalyst precursor (**G1**) under reduced pressure to remove the ethylene byproduct from the reaction equilibrium (Table 1). Polymerization temperatures were increased stepwise from 50 °C to temperatures between 65 °C (for copolymers with low ketone contents) and 100 °C (for the homopolymer of **1**) to prevent the reaction mixtures from solidifying. Unsaturated polyketones with contents between 52.6 groups per 1000 methylene units (from homopolymerization of **1**) and 0 ketone groups (from homopolymerization of **2**) were obtained. The compositions of all polyketones were found to be identical with the initial monomer ratios, as determined by the ratios of signal intensities for the methylene units adjacent to the ketone functionalities to all proton resonances from the ^1H NMR spectra. The unsaturated copolymers were hydrogenated with H_2, applying the Fischer carbene generated by quenching **G1** with a large excess of ethyl vinyl ether as a hydrogenation catalyst precursor.[19] Complete hydrogenation of the carbon–carbon double bonds was confirmed by the absence of signals for olefinic protons by high temperature ^1H NMR spectroscopy. Molecular weights were analyzed by GPC and ^1H NMR spectroscopy via end-group signal integration to yield absolute molecular weights (M_n). Molecular weights on the order of 5000–10000 g mol^{-1} and molecular weight distributions M_w/M_n around 2 were observed for most copolymers, as expected for well-behaved polycondensation reactions (Table 1). In addition, the ^1H NMR spectra confirm the anticipated strictly linear microstructure.

For unsaturated polyketones melting points increase from values between 40 and 50 °C for compounds with low degrees of ketone functionalization to 95 °C for the homopolymer of **1** (52.6 ketone groups per 1000 CH_2 units, see Figure 1, Table 1, and Supporting Information). Hydrogenation resulted in much enhanced melting temperatures to values between 125 and 134 °C. This data illuminates the convergence of polyketones toward linear polyethylene with decreasing functional group contents. The comparison with the melting data of ethylene/CO copolymers reported by Müller and co-workers shows differences of 5–10 °C,[11] displaying the relevant impact of additional methyl branches on the melting properties.

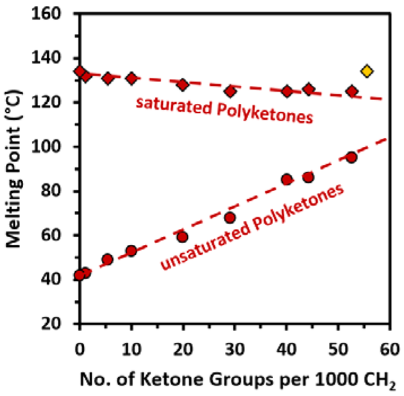


Figure 1. Peak melting points of unsaturated random polyketones (red circles) generated by ADMET copolymerizations and saturated polyketones (red diamonds) after hydrogenation, together with the regular polyketone (yellow diamond) reported by Watson and Wagener.[18]

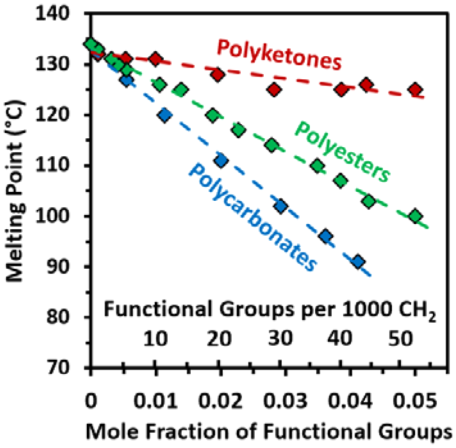


Figure 2. Melting points of long-spaced polyketones (red; this study), polyesters[16] (green), and polycarbonates[17] (blue) vs the mole fraction of functional groups.

A difference between the melting points of randomly spaced polyketones from ADMET copolymerizations and the regularly spaced polyketone reported by Watson and Wagener becomes obvious (Figure 1).[18] Related observations have previously been made for polyesters and polycarbonates, where regular compounds from classical $A_2 + B_2$ polycondensations generally melt at higher temperatures than their randomly spaced congeners with comparable functional group contents (vide infra).[16,17]

The crystalline properties of saturated polyketones were further analyzed by wide-angle X-ray diffraction (WAXD, cf. Supporting Information). WAXD patterns of polyketones show only slight shifts of the dominant reflexes compared to linear polyethylene, displaying crystallization in the orthorhombic crystal structure, where hydrocarbon chains are parallelly arranged in an all-*trans* conformation and the ketone groups are built into the crystalline phase. To describe the melting behavior of random polyketones, the Sanchez-Eby inclusion model[20] appears reasonable (as previously found for random polyesters[16,21] and polycarbonates[17]). In a copolymer consisting of A and B building blocks, this model regards B units (here: ketone groups) as defect units included in a lattice of crystalline A units (CH_2). Applied to random polyketones, the melting point depression with respect to the mole fraction of functional groups should follow the relationship

$$T_m = T_m^0\left(1 - \frac{\varepsilon}{\Delta H_m^0}X_K - \frac{2\sigma}{\Delta H_m^0 l}\right)$$

where T_m is the melting temperature of the copolymer, $T_m{}^0$ is the equilibrium melting temperature, $\Delta H_m{}^0$ is the heat of fusion for linear polyethylene, X_K is the mole fraction of ketones (as disturbing units), σ is the surface free energy of the crystal, and l is the lamellae thickness. Incorporated defect units create an energy penalty ε, which reduces the crystal packing energy by the defect free energy.[22] Indeed, the melting points of polyketones plotted against the mole fraction of ketone groups follow the linear relationship of $T_m = (132 - 172 \times X_K)$ °C (Figure 2).

The comparison of random polyketones with polyesters and polycarbonates containing the same degrees of functionalization illustrate the very different melting properties following T_m (polyketones) > T_m (polyesters) > T_m (polycarbonates), though all these carbonyl moieties are easily incorporated into polyethylene-like lattices. However, these carbonyl groups vary significantly in their polarities.[23,24] The different slopes in the linear melting regressions can be related to different abilities for polar group layer formation within the crystalline phase. As intensively studied for polyesters,[25,26] layering of the polar disturbing units in the crystalline phase can generate defect-free areas of pure hydrocarbon chains, increasing the overall cohesion energy. The high melting points of random polyketones can be attributed to the stronger polarity of ketone groups compared to ester and carbonate moieties, facilitating ketone layer formation. The same considerations can explain the higher melting points of regularly spaced carbonyl functionalized polymers compared to their randomly spaced congeners (compare Figure 1).

In conclusion, the long-spaced random polyketones prepared can act as accurate models for linear ethylene/CO copolymers with CO incorporations in the relevant regime of 9.5 mol % and lower. Melting points for defect-free polyketones derived from ADMET copolymerizations are observed several degrees above reported values for ethylene/CO copolymers, being related to the additional disturbing effects of methyl branching in the latter. Compared to other long-spaced main-chain functionalized polymers, the polyketones studied here are an extreme case, in that the polarity of the ketone group is high. The melting behavior observed underlines the picture, that the disturbing effect of the functional groups on polyethylene crystallization can be partially compensated by polar interactions between the functional groups.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and methods, detailed synthetic procedures, NMR spectra, T_m, T_c, and ΔH data, DSC traces, and WAXD patterns of saturated polyketones. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00324.

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Notes

The authors declare no competing financial interest.

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