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Palladium(II)-Catalyzed Synthesis of Alternating Fluoroalkene−Carbon Monoxide Copolymers

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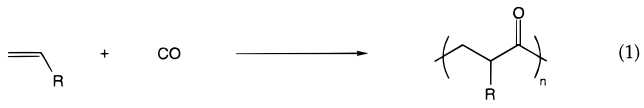
ABSTRACT: The cationic palladium(II) complex [(R,R-Me-DuPHOS)Pd(Me)(CH_3CN)]$^+BF_4^-$ (R,R-Me-DuPHOS = 1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene) was found to catalyze the perfectly alternating copolymerization of fluorinated allylbenzene derivatives with carbon monoxide, leading to functional polymers containing pendant fluorinated groups. The copolymers each exhibited relatively high hydrophobicity, as determined by goniometry. The *alt*-allylpentafluorobenzene−carbon monoxide copolymer was found to significantly increase the water contact angle of poly(methyl methacrylate) when blended in small amounts with the latter.

Introduction

The copolymerization of alkenes with carbon monoxide has been well-documented (eq 1)[1] and is of interest



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due to (a) the ready availability and low cost of the comonomers, particularly carbon monoxide, and (b) the presence of the carbonyl functionality in the backbone which provides an avenue for further functionalizations. Through the use of transition-metal catalysts bearing chiral ligands, isotactic and optically active alkene−carbon monoxide copolymers have been synthesized,[2,3] including an optically active allylbenzene−carbon monoxide copolymer.[2a] This report describes the synthesis of copolymers of carbon monoxide and fluorinated allylbenzene derivatives. One goal of this project was to obtain polymers that could be blended in small amounts with polar polymers such that the surface properties of the latter were altered. Such a modification could provide a material with the mechanical properties of the polar polymer, as well as the chemical resistance of the fluorinated polymer. In addition, fluorinated polyketones have potential as a new family of compatibilizers for blends of polar and fluorinated polymers.

Results and Discussion

Monomer Synthesis. Monomers **1**−**5** (Figure 1)

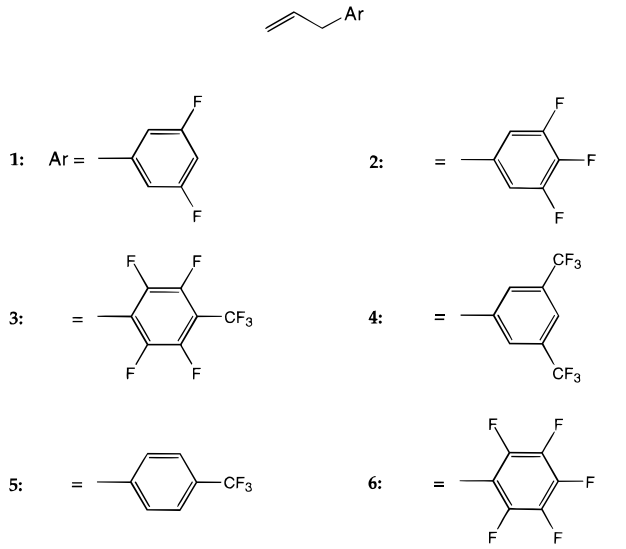

Figure 1. Fluorinated alkene monomers.

were synthesized by conventional aryl Grignard chemistry, as depicted in eq 2. Two-phase liquid workup followed by vacuum distillation afforded the pure products in good yields. The syntheses of **4**[4] and **5**[3] have been previously reported, while **6** is commercially available.

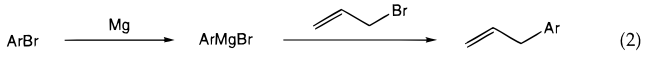

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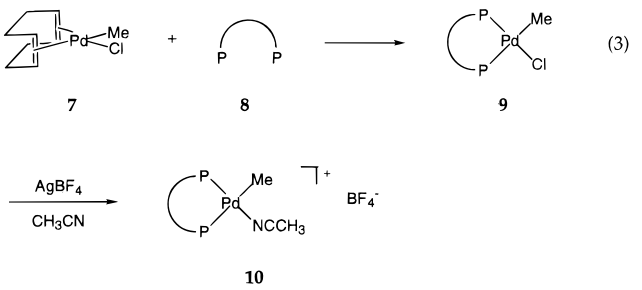
Table 1. Copolymerization of Fluorinated Alkenes with Carbon Monoxide[a]

copolymer	yield,[b] %	M_n[c]	M_w[c]	M_w/M_n[c]	water contact angle (deg)	T_m (°C)
1−CO	76	5550	9 610	1.73	89	208
2−CO[d]	77	6000	10 800	1.80	96	237
3−CO	17				97	227
4−CO	65	9170	16 500	1.80	88	220
5−CO[d]	75	7360	11 300	1.54	93	216
6−CO	41	2130[e]	2 450[e]	1.15[e]	96	*f*

[a] Conditions: 5 g of alkene monomer, 0.2 mol % **10**, 500 psi of CO, 20−30 mL of $CHCl_3$, 60 °C, 2 days. [b] Based on amount of alkene monomer used. [c] Determined by GPC in THF solvent, relative to polystyrene standards. [d] 3 day reaction. [e] Determined by GPC in $CHCl_3$ solvent relative to polystyrene standards; a trace amount of the copolymer did not dissolve in $CHCl_3$. [f] No distinct melting peak was observed.

Catalyst. The catalyst used for the alternating copolymerization was [(R,R-Me-DuPHOS)Pd(CH_3)CH_3-CN]$^+BF_4^-$ (**10**). It was prepared according to eq 3, in which **7** underwent ligand exchange with (−)-1,2-bis-(2*R*,5*R*)-2,5-dimethylphospholanobenzene (R,R-Me-DuPHOS) (**8**) to form the neutral chloride complex **9**. The neutral complex then underwent metathesis with $AgBF_4$ in the absence of light to form the cationic catalyst **10.**



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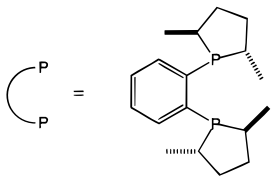
7 **8** **9**

10



1,2-Bis(2R,5R)-dimethylphospholanobenzene

(R,R)-Me-DuPHOS

Palladium(II)-Catalyzed Synthesis of Fluorinated Alkene−Carbon Monoxide Copolymers. Complex **10** catalyzed the synthesis of copolymers of carbon monoxide with each of the alkenes **1**−**6**. The synthesis of the **5**−CO copolymer has previously been reported; a different palladium catalyst was used.[3] Our results are shown in Table 1. It is apparent that the use of more fluorinated monomers resulted in lower yields of copolymer. For example, **1** has only two fluorine atoms and gave a 76% copolymer yield, while **3** has seven fluorine atoms and gave only a 17% copolymer yield. A possible reason for this discrepancy is the lowered ability of the more fluorinated, and therefore more electron-withdrawing, monomer to coordinate to the palladium center.

None of the copolymers were soluble in halogenated organic solvents with the exception of **6**−CO copolymer. Copolymers **1**−, **2**−, **4**−, and **5**−CO were soluble in THF, which is not surprising when one considers the structural similarity of THF and the spiroketal portion of the copolymer (vide infra). **3**−CO copolymer was insoluble in common organic solvents. Solubility became an important issue where polymer blends were concerned (vide infra).

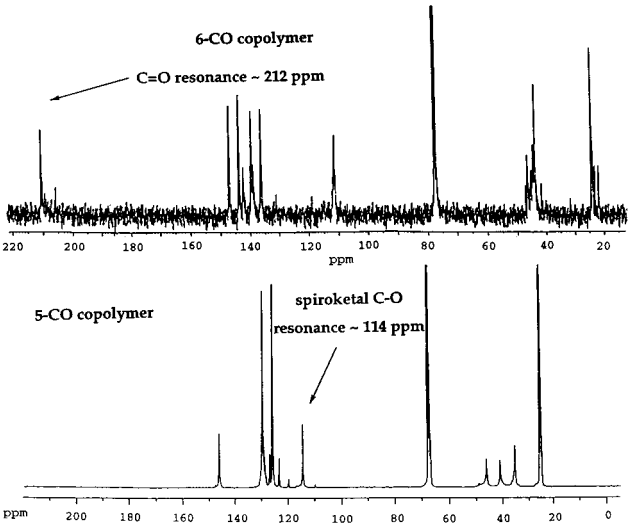


Figure 2. $^{13}C\{^1H\}$ NMR spectra of selected fluorinated alkene−CO copolymers.

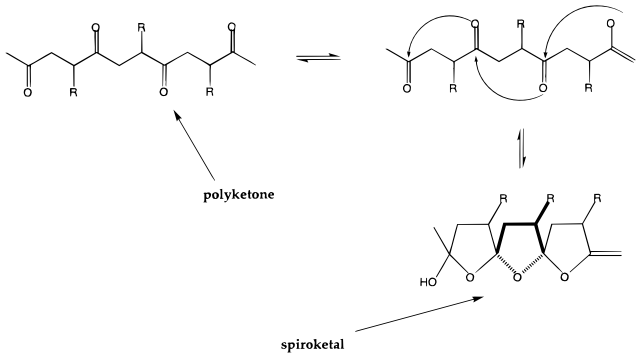


Figure 3. Proposed mechanism for spiroketal formation.

Nuclear Magnetic Resonance Spectroscopy of Fluorinated Alkene−CO Copolymers. The ^1H NMR (THF-d_8) spectra of **1**−, **2**−, **4**−, **5**−, and **6**−CO copolymers (in $CDCl_3$) are very similar. The backbone protons resonate as a collection of broad peaks between 1.6 and 3.5 ppm. There are also two broad, low-intensity resonances at approximately 1.2 and 0.8 ppm, which may correspond to alkyl end groups. Aromatic protons resonate between 6.3 and 8 ppm, depending on the fluorine substitution on the aromatic ring.

The ^{13}C NMR spectra of **1**−, **2**−, **4**−, **5**−, and **6**−CO copolymers (THF-d_8) (see Figure 2 for representative spectra) provide insight concerning the nature of the polymer backbone. It is well-known that 1,4-polyketone synthesized from an 1-alkene comonomer can isomerize to poly(spiroketal)[2a] (Figure 3). The spiroketal linkage consists of a stable five-membered ring and is often the favored form of the copolymer. As synthesized, the keto group was present in all the copolymers, exhibiting a chemical shift of approximately 212 ppm. Furthermore, the presence of only one set of carbonyl absorptions confirms an exclusive head-to-tail structure for the copolymers.[2a,b] Aside from the aromatic carbons, the remainder of the ^{13}C NMR spectra consist of aliphatic carbon resonances below 50 ppm, due to the backbone CH, backbone CH_2, and benzylic CH_2 groups. Differentiation of the backbone carbons was accomplished

by examination of the DEPT-135 ^{13}C NMR data.

While IR data (vide infra) confirm the existence of keto groups in the copolymers, ^{13}C NMR spectra for **1**−, **2**−, and **4**−CO copolymers suggest the presence of spiroketal units, as evidenced by a resonance at approximately 114−118 ppm (see Figure 2). Spiroketal formation cannot be unequivocally asserted for the above-mentioned copolymers due to overlapping peaks from aromatic carbons in that region. In the same vein, the resonance at 112 ppm observed for **6**−CO copolymer (see Figure 2) is due to the ipso carbon in the aromatic ring and not due to spiroketal linkages; a similar resonance is exhibited by the monomer **6** at 113 ppm. In the case of the **5**−CO copolymer, the keto groups isomerized in the solid state over several months to give a polymer with purely spiroketal linkages (Figure 2).

Infrared Spectroscopy. The key absorption in the IR spectra of all the copolymers is at approximately 1708 cm^{-1} and corresponds to the C═O stretch of the keto group in the polymer backbone. While the C═O absorption is initially present for all of the copolymers (the C═O units completely disappeared over time for **5**−CO copolymer, vide supra), it is not a strong signal in any case (excepting **6**−CO copolymer, which is a pure 1,4-polyketone). This observation lends weight to the possible presence of spiroketal units (vide supra). The spiroketal unit typically exhibits an absorption at ca. 750 cm^{-1}, but it is not apparent from the spectra whether this signal corresponds to the spiroketal unit, as it is also not very intense and may correspond to groups other than spiroketal.

Differential Scanning Calorimetry. All of the copolymers except **6**−CO copolymer clearly exhibited crystalline melt behavior with T_m varying from 200 to 240 °C, as determined by differential scanning calorimetry. It is interesting to note that the melting peak for each of the crystalline copolymers had a shoulder. The two peaks may signify polyketone repeat units as well as runs of spiroketal linkages (vide supra). It should be noted that an alkene−CO copolymer containing both ketone and spiroketal units is likely to have a "blocky" microstructure[5] because of the tandem nature of the isomerization (Figure 3).

Interestingly, **6**−CO was the only copolymer synthesized that exhibited no crystallinity; the amorphous character of the copolymer was confirmed by powder X-ray diffraction. It was also the only copolymer of those tested that caused a dramatic change in surface behavior when blended with poly(methyl methacrylate) (vide infra). In addition, it was the only copolymer that was soluble in halogenated organic solvents and not just THF, presumably due to its amorphous nature and/or pure polyketone content. The reason for the lack of crystallinity of **6**−CO copolymer is not clear; it may be a consequence of the lack of rigid spiroketal blocks in the backbone.

Optical Rotation Measurements. The alternating 1-alkene−carbon monoxide copolymers have stereogenic centers in the polymer backbone. At the high molecular weight limit, a *syndiotactic* alternating 1-alkene−carbon monoxide copolymer chain will always show vanishingly small optical activity since the absolute configuration of the stereogenic centers in the backbone *alternates* (i.e., ...RSRSRS...). On the other hand, the stereogenic centers in the individual chains of an *isotactic* alternating 1-alkene−carbon monoxide copolymer sample have the *same* absolute configurations (i.e., ...RRRRRR... or ...SSSSSS...), and thus, the synthesis of optically active, isotactic alternating 1-alkene−carbon monoxide copolymers is feasible.[2,3] Since a chiral catalyst was employed to effect the copolymerizations, there existed the possibility of the formation of isotactic polymers showing optical activity. Indeed, the **6**−CO copolymer was analyzed by polarimetry and showed an optical rotation of $[\Phi]_D^{25} = +87°$ (c = 50 mg/mL, $CHCl_3$). The high degree of isotacticity associated with the observed optical activity was further evident from the ^{13}C NMR spectrum of the copolymer (Figure 2). From a single dominant resonance for the carbonyl group, we estimate that the degree of tacticity was over 90%.[2a]

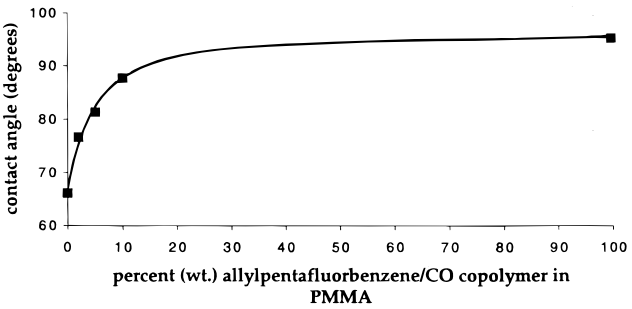


Figure 4. Dependence of water contact angle on amount of **6**−CO copolymer blended in PMMA.

On the other hand, when the copolymers of carbon monoxide and **1**, **2**, **4**, and **5** were analyzed in THF solution, the optical rotations were low enough to be within the error limits of the polarimeter. The reason for the relatively high optical rotation in the case of **6**−CO copolymer is that it is the only copolymer containing purely 1,4-ketone (as opposed to spiroketal) repeat units. It has been shown that chiral poly(spiroketals) generally exhibit low optical rotations compared to those of the corresponding polyketones.[2a] The low optical rotations are further support for the existence of a large concentration of spiroketal units in those copolymers.

Contact Angle Studies. Solution-cast films of the copolymers of carbon monoxide with **1**−**6** were examined for their water contact angle, as determined by goniometry. As can be seen from Table 1, the contact angle generally increases with increasing fluorine content.

As shown in Table 2, **6**−CO copolymer and polystyrene have nearly the same hydrophobicity. However, when 10 wt % **6**−CO copolymer was blended with poly(methyl methacrylate) (PMMA), the water contact angle of the blend increased by 22°. On the other hand, blending in a similar amount of polystyrene with PMMA resulted in virtually no change in water contact angle. The reason for this large difference is not precisely known, but it is hypothesized that the polyketone oxygen atoms interact with the polar groups of PMMA to orient the hydrophobic perfluorinated phenyl substituent toward the surface. Figure 4 shows the dependence of the water contact angle on the amount of **6**−CO copolymer in the PMMA blend and indicates that the hydrophobicity of the blend increases rapidly with increasing **6**−CO copolymer concentration.

To examine the possibility of phase separation in the blends of **6**−CO copolymer with PMMA, scanning electron microscope (SEM) images were obtained for a 1:1 (wt) blend of PMMA and the copolymer. The sample was stained with RuO_4 to identify aromatic groups. The analog dot map generated by X-ray microanalysis and the SEM secondary emission image are shown in Figure

Table 2. Contact Angle (deg) Data

	water contact angle
polymer	
polystyrene (PS)	94
poly(methyl methacrylate) (PMMA)	66
copolymer	
6−CO	96
allylbenzene−CO (nonfluorinated)	83
polymer blend	
10% PS in PMMA	67
10% **6**−CO in PMMA	88

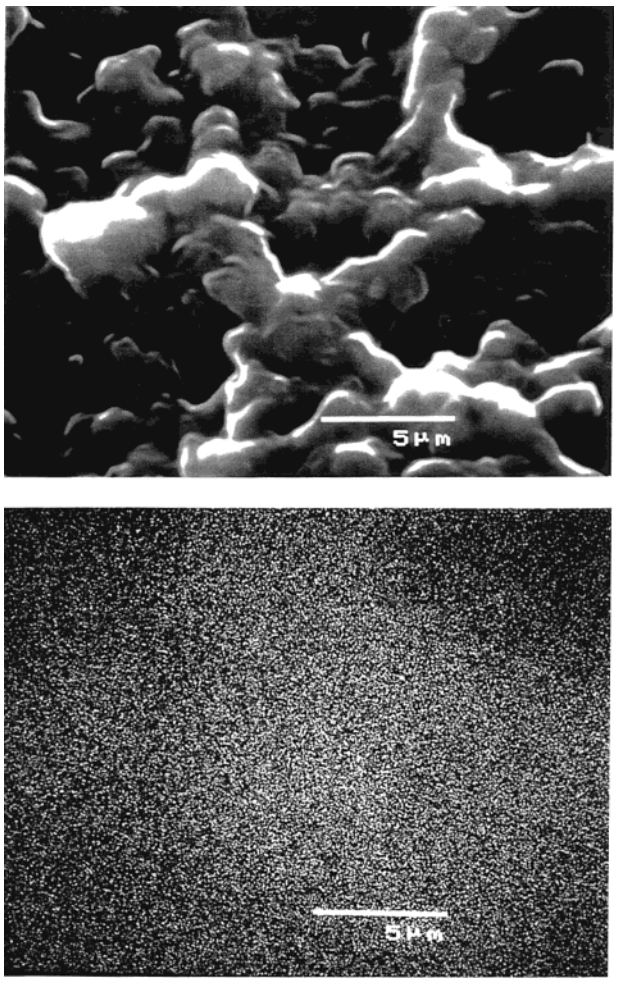


Figure 5. Scanning electron micrographs of a 1:1 (wt) PMMA: **6**−CO copolymer blend (20 kV, ×7500 magnification): (a, top) SEM secondary emission image; (b, bottom) analog dot map. (Scale bar = 5 μm.)

5. As the dot map reveals, the ruthenium stain is distributed evenly throughout the sample, thereby indicating the absence of phase separation on a micron scale.

The copolymers of carbon monoxide with **1**−**5** were also blended with PMMA. However, they did not cause any increase in the water contact angle of the blends as **6**−CO copolymer did. The reason for this behavior is most likely due to the much higher concentration of spiroketal units in the copolymers of **1**−**5** with carbon monoxide. A spiroketal unit may not interact with the polar groups of PMMA in the same manner as the more polarized keto group.

Experimental Section

Materials. All chemicals were used as received unless otherwise noted. Oakwood supplied 1-bromo-3,4,5-trifluorobenzene, which was dried over molecular sieves before use. Aldrich supplied 1-bromo-3,5-difluorobenzene, 1-bromo-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene, and allyl bromide, which were dried over molecular sieves before use. Polystyrene and poly(methyl methacrylate) were also obtained from Aldrich, as was allylpentafluorobenzene, which was dried over molecular sieves and freeze−thaw degassed prior to use. Silver tetrafluoroborate and 1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene (R,R-Me-DuPHOS) were purchased from Strem Chemicals. Magnesium turnings were supplied by Johnson Matthey. (1,5-Cyclooctadiene)Pd(Me)Cl was prepared according to a literature preparation,[6] as were **4**[4] and **5**.[3] Ether was dried over sodium benzophenone ketyl and distilled under nitrogen prior to use. Methylene chloride, chloroform, and acetonitrile were dried over calcium hydride, distilled under nitrogen or vacuum, and freeze−thaw degassed prior to use. C. P. grade carbon monoxide was purchased from Matheson or MG Industries. All fluorinated alkene monomers were dried over molecular sieves and freeze−thaw degassed prior to use.

General Methods. All catalyst preparations and copolymerization setups were performed in a nitrogen-filled glovebox. All copolymerizations were run in a 125 mL stainless steel autoclave equipped with a glass liner and Teflon-coated stir bar. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM-300 (later upgraded to DPX-300) or WP-200 spectrometer. ^{1}H and ^{13}C resonances were referenced to residual protic impurities in $CDCl_3$ (7.27 ppm for ^{1}H, 77.23 ppm for ^{13}C) or THF (3.58 ppm for ^{1}H, 67.57 ppm for ^{13}C). ^{31}P resonances were referenced to external 85% phosphoric acid in water. ^{19}F NMR spectra were recorded on a Bruker WP-200 spectrometer and were referenced to external hexafluorobenzene (−163 ppm). IR spectra were obtained on a Perkin-Elmer 1600 FT-IR spectrophotometer. Water contact angles were measured on a Ramé-Hart contact angle goniometer. Thermal analyses were performed on a Perkin-Elmer DSC7 differential scanning calorimeter under an argon purge. A 20 °C/min heating rate was used. Optical rotations were obtained on a Perkin-Elmer 241 polarimeter with a sodium lamp. Molecular weights were measured in $CHCl_3$ on a Waters gel permeation chromatograph equipped with Styragel columns and a differential refractometer detector or in THF (containing 0.01 M tetrabutylammonium nitrate) on a Hewlett-Packard 1090 gel permeation chromatograph equipped with Phenominex Phemgel columns and a differential refractometer detector. Polystyrene standards were used for calibration. Elemental analyses were provided by Quantitative Technologies, Inc. (Whitehouse, NJ). Scanning electron microscopy (SEM) and energy dispersive spectroscopy were performed on a JEOL 5400 SEM equipped with a standard detector (Princeton Gamma-Tech-PGT, Princeton, NJ). Spectra were collected using a 20 kV accelerating voltage and a takeoff angle of 30°. PGT's IMIX system (v. 7) was used for X-ray microanalysis and mapping. Samples were prepared by dissolving the two polymers in chloroform, evaporating the solvent, and exposing the resulting film to RuO_4 vapor for 1 h in sealed nested glass dishes in a fume hood. Films were mounted onto an aluminum stub with double-sided carbon tape and evaporated with three 1 s bursts of carbon in a BAL-TEC SCD-050 coater (Techno Trade, Boston, MA). Photographs were recorded on Polaroid 55 film (ISO-50).

Synthesis of (R,R-Me-DuPHOS)Pd(Me)(Cl), 9. A solution of R,R-Me-DuPHOS (50 mg, 0.163 mmol) in 4 mL of methylene chloride was added to a solution of (1,5-cyclooctadiene)Pd(Me)(Cl) (42 mg, 0.158 mmol) in 4 mL of methylene chloride. The beige solution was stirred 20 h at room temperature and then was filtered through a fine frit. The filtrate was evaporated to yield a beige solid (70 mg, 96%). ^{1}H NMR ($CDCl_3$) (ppm): 7.70−7.54 (m, *Ar*), 3.12 (m), 2.93 (m), 2.65 (m), 2.31 (m), 1.80 (m), 1.41 (ddd, J = 6.9 Hz, J = 18.9 Hz, J = 47.4 Hz), 0.85 (ddd, J = 7.2 Hz, J = 15.9 Hz, J = 24.9 Hz), 0.61 (dd, $^3J_{HP}$ = 2.7 Hz, $^3J_{HP}$ = 7.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$) (ppm): 144.9 (dd, J = 37.9 Hz, J = 46.9 Hz), 142 (dd, J = 26.3 Hz, J = 30.0 Hz), 132.9 (pseudo dd), 131.2 (m), 41.7 (pseudo dd), 37.4 (m), 35.7 (d, J = 17.8 Hz), 28.2 (s), 17.5 (pseudo tr), 14.5 (d, J = 27.5 Hz), 6.2 (d, J = 109.7 Hz). ^{31}P{^{1}H} NMR

($CDCl_3$) (ppm): 79.4 (d, $^2J_{PP}$ = 25.1 Hz), 69.8 (d, $^2J_{PP}$ = 25.0 Hz).

Synthesis of [(R,R-Me-DuPHOS)Pd(Me)(CH_3CN)]$^+BF_4^-$, 10. Complex **9** (70 mg, 0.151 mmol) was dissolved in 7 mL of methylene chloride. A solution of $AgBF_4$ (31 mg, 0.159 mmol) in 3 mL of acetonitrile was added, and gray precipitate formed. The mixture stirred at room temperature in the absence of light for 3 h and then was filtered through a fine frit. The filtrate was evaporated to yield a light brown solid (71 mg, 85%). ^{1}H NMR ($CDCl_3$) (ppm): 7.70 (br, *Ar*), 2.85 (m), 2.44 (m), 1.80 (m), 1.38 (dt, J = 19.7 Hz, J = 7.0 Hz), 0.89 (ddd, J = 7.1 Hz, J = 16.7 Hz, J = 23.9 Hz), 0.53 (dd, $^3J_{HP}$ = 1.7 Hz, $^3J_{HP}$ = 7.1 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$) (ppm): 142.7 (t, J = 44.0 Hz), 132.3 (t, J = 33.6 Hz), 42.2 (d, J = 33.6 Hz), 40.6 (d, J = 18.9 Hz), 38.4 (d, J = 32.1 Hz), 37.0 (m), 18.2 (d, J = 12.4 Hz), 17.4 (d, J = 6.9 Hz), 5.4 (s), 2.8 (s). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 79.7 (d, $^2J_{PP}$ = 25.0 Hz), 69.9 (d, $^2J_{PP}$ = 25.3 Hz).

Synthesis of 3,5-Difluoroallylbenzene, 1. Magnesium turnings (4.26 g, 176 mmol) were charged to 150 mL of ether in a three-neck round-bottom flask equipped with reflux condenser and addition funnel. A few iodine crystals were added to serve as an indicator for Grignard reagent formation. A solution of 1-bromo-3,5-difluorobenzene (16.91 g, 88 mmol) in 10 mL of ether was added dropwise over 20 min with stirring. The mixture turned deep brown-red and self-refluxed after 25 min. The liquid was cannulated into another three-neck flask equipped with reflux condenser and addition funnel. A solution of allyl bromide (7.4 mL, 8.88 mmol) in 10 mL of ether was added dropwise, and the solution was heated to reflux for 18 h, after which a light colored precipitate had formed. The product mixture was poured onto ice and diluted with 50 mL of ether, and the organic layer was washed with water (3 × 100 mL). The organic layer was dried over anhydrous magnesium sulfate and filtered through a plug of silica gel. The ether was fractionally distilled off at atmospheric pressure. The remaining liquid was diluted with mineral oil (to prevent distillation to dryness), and the product was fractionally distilled under vacuum to afford a colorless liquid (6.92 g, 52%). Bp 23 °C (0.12 Torr). ^{1}H NMR ($CDCl_3$) (ppm): 6.82−6.59 (m, 3H, CH_2=CHCH_2*Ar*), 6.03−5.82 (m, 1H, CH_2=C*H*CH_2Ar), 5.27−5.07 (m, 2H, C*H*$_2$=CHCH_2Ar), 3.38 (d, 2H, CH_2=CHC*H*$_2$Ar), $^3J_{HH}$ = 6.60 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$) (ppm): 163.28 (dd, CH_2=CHCH_2Ar_{meta}, $^3J_{CF}$ = 12.93 Hz, $^1J_{CF}$ = 247.8 Hz), 144.21 (t, CH_2=CHCH_2Ar_{ipso}, $^3J_{CF}$ = 8.86 Hz), 135.94 (s, *C*H$_2$=CHCH$_2$Ar), 117.28 (s, CH_2=*C*HCH$_2$Ar), 111.53 (m, CH_2=CHCH_2Ar_{ortho}), 101.75 (t, CH_2=CHCH_2Ar_{para}, $^2J_{CF}$ = 25.41 Hz), 39.92 (s, CH_2=CH*C*H$_2$Ar). ^{19}F{^{1}H} NMR ($CDCl_3$) (ppm): −107.06 (s). IR (KBr, cm^{-1}): 3084, 2980, 2913, 1845, 1627, 1594, 1461, 1319, 1115, 987, 916, 845. MS (EI, *m*/*z*): 153, 143, 127, 115, 101, 69, 44, 32.

Synthesis of 3,4,5-Trifluoroallylbenzene, 2. The procedure was identical to that of **1**, except 1-bromo-3,4,5-trifluorobenzene was the aryl halide used. Colorless liquid was yielded (76%). Bp 24 °C (0.12 Torr). ^{1}H NMR ($CDCl_3$) (ppm): 6.80 (pseudo tr, 2H, CH_2=CHCH_2*Ar*), 5.95−5.82 (m, 1H, CH_2=C*H*CH_2Ar), 5.17−5.08 (m, 2H, C*H*$_2$=CHCH_2Ar), 3.33 (d, 2H, CH_2=CHC*H*$_2$Ar, $^3J_{HH}$ = 6.60 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$) (ppm): ^{19}F {^{1}H} NMR ($CDCl_3$) (ppm): −131.63 (d, 2F, CH_2=CHCH_2Ar_{meta}, $^3J_{FF}$ = 20.89 Hz), −160.89 (t, 1F, CH_2=CHCH_2Ar_{para}, $^3J_{FF}$ = 19.57 Hz). IR (KBr, cm^{-1}): 3084, 2980, 2913, 1850, 1618, 1528, 1442, 1347, 1234, 1044, 992, 921. MS (EI, *m*/*z*): 172, 145, 131, 91, 69, 51, 45, 40, 32.

Synthesis of 2,3,4,5-Tetrafluoro-4-(trifluoromethyl)-allylbenzene, 3. The procedure was identical to that of **1** except 1-bromo-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene was the aryl bromide used. Colorless liquid was yielded (60%). Bp 24 °C (0.12 Torr). ^{1}H NMR ($CDCl_3$) (ppm): 5.97−5.83 (m, 1H, CH_2=C*H*CH_2Ar), 5.19−5.11 (m, 2H, C*H*$_2$=CHCH_2Ar), 3.54 (d, 2H, CH_2=CHC*H*$_2$Ar, $^3J_{HH}$ = 6.34 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$) (ppm): 147.8−146.6 (dm), 143.2−141.7 (dm), 132.1 (s, CH_2=*C*H-CH_2Ar), 123.4 (t, J_{CF} = 18.27 Hz), 118.2 (s, *C*H$_2$=CHCH$_2$Ar), 27.3 (s, CH_2=CH*C*H$_2$Ar). ^{19}F {^{1}H} NMR ($CDCl_3$) (ppm): −52.79 (t, 3F, C*F*$_3$, $^4J_{FF}$ = 21.27 Hz), −137.87 (d, 2F, CH_2=CHCH_2Ar_{ortho}, $^3J_{FF}$ = 12.23 Hz), −138.61 (d, CH_2=CHCH_2Ar_{meta}, $^3J_{FF}$ = 9.98 Hz). IR (KBr, cm^{-1}): 3094, 2990, 1855, 1665, 1641, 1494, 1409, 1333, 1181, 992, 911, 864. MS (EI, *m*/*z*): 258, 239, 231, 189, 163, 69, 41, 32.

Synthesis of *alt*-1−CO Copolymer. A glass autoclave liner equipped with a Teflon-coated stir bar was charged with **10** (36 mg, 0.065 mmol), which was dissolved in 30 mL of chloroform. Monomer **1** (5.00 g, 32.5 mmol) was then added. The liner was placed in a 125 mL stainless steel autoclave, which was charged to 500 psi with carbon monoxide. The mixture stirred in a 60 °C oil bath for 2 days. The autoclave was then vented of excess carbon monoxide, and the product mixture was poured into 1.5 M methanolic HCl, filtered, washed with methanol, and dried under vacuum to yield a white powdery solid (4.45 g, 76%). Anal. Calcd for $(C_{10}H_8F_2O)_n$: 65.9% C, 4.4% H, 20.9% F. Found: 63.9% C, 4.4% H, 20.9% F. ^{1}H NMR (THF-d_8) (ppm): 7.3−6.3 (br, *Ar*), 3.4−1.6 (br, *aliphatic*), ^{13}C{^{1}H} NMR (THF-d_8) (ppm): 211.3 (s, *C*=O), 164.0 (dd, Ar_{meta}, $^4J_{CF}$ = 12.81 Hz, $^1J_{CF}$ = 247.4 Hz), 145.0 (d, Ar_{ipso}, $^3J_{CF}$ = 86.1 Hz), 116.8−112.3 (m, Ar_{ortho} + spiroketal *C*−O), 103.1−101.9 (m, Ar_{para}), 47.3−45.7 (m, backbone *C*H$_2$), 41.3−40.5 (br, backbone *C*H), 37.6 and 35.6 (br, benzylic *C*H$_2$). ^{19}F{^{1}H} NMR (THF-d_8) (ppm): −107.47 (br), −107.84 (br). IR (KBr, cm^{-1}): 2919, 1708, 1619, 1590, 1461, 1308, 1114, 973, 814.

Synthesis of *alt*-2−CO Copolymer. The procedure was analogous to that of **1**−CO copolymer. White powdery solid was yielded (77%). Anal. Calcd for $(C_{10}H_7F_3O)_n$: 60.0% C, 3.5% H, 28.5% F. Found: 59.9% C, 3.4% H, 28.5% F. ^{1}H NMR (THF-d_8) (ppm): 7.2−6.5 (br, *Ar*), 3.4−1.5 (br, *aliphatic*). ^{13}C{^{1}H} NMR (THF-d_8) (ppm): 211.8, (s, *C*=O), 151.5 (d, $^1J_{CF}$ = 250.33 Hz), 141.7−135.7 (br, Ar_{ipso} + Ar_{para}), 115.4−112.2 (br m, Ar_{ortho}), 48.8−45.8 (br, backbone *C*H), 37.6 (s, backbone *C*H$_2$), 35.5 (s, backbone *C*H). ^{19}F{^{1}H} NMR (THF-d_8) (ppm): −130.87 (br, 2F, Ar_{meta}), −158.38 (br, 1F, Ar_{para}). IR (KBr, cm^{-1}): 2931, 1702, 1614, 1531, 1449, 1349, 1232, 1038, 950, 838, 732.

Synthesis of *alt*-3−CO Copolymer. The procedure was analogous to that of **1**−CO copolymer. White powdery solid was yielded (17%). Anal. Calcd for $(C_{11}H_5F_7O)_n$: 46.2% C, 1.8% H, 46.5% F. Found: 46.4% C, 1.8% H, 46.3% F. ^{1}H NMR (THF-d_8) (ppm): 7.2−6.5 (br, *Ar*), 3.4−1.5 (br, *aliphatic*). IR (KBr, cm^{-1}): 2931, 1708, 1655, 1490, 1402, 1331, 1220, 1143, 955, 861, 826, 709.

Synthesis of *alt*-4−CO Copolymer. The procedure was analogous to that of **1**−CO copolymer. White powdery solid was yielded (65%). Anal. Calcd for $(C_{12}H_8F_6O)_n$: 51.1% C, 2.9% H, 40.4% F. Found: 48.0% C, 2.8% H, 37.6% F. ^{1}H NMR (THF-d_8) (ppm): 8.0−7.2 (br, *Ar*), 3.5−1.6 (br, *aliphatic*). ^{13}C{^{1}H} NMR (THF-d_8) (ppm): 211.4 (s, *C*=O), 142.3 (s), 134.2−131.7 (br), 130.9 (s, *Ar*), 130.6−129.3 (br), 124.7 (d, Ar_{CF}, J_{CF} = 264.67 Hz), 121.697 (s), 47.0 (s, backbone *C*H), 45.1 (s, backbone *C*H$_2$), 37.2 (benzylic *C*H$_2$). ^{19}F{^{1}H} NMR (THF-d_8) (ppm): −62.19 (br). IR (KBr, cm^{-1}): 2931, 1708, 1655, 1490, 1402, 1331, 1220, 1143, 955, 861, 826, 709.

Synthesis of *alt*-5−CO Copolymer. The procedure was analogous to that of **1**−CO copolymer. White powdery solid was yielded (75%). Anal. Calcd for $(C_{10}H_7F_3O)_n$: 61.7% C, 4.2% H, 26.6% F. Found: 61.4% C, 4.2% H, 26.8% F. ^{1}H NMR (THF-d_8) (ppm): 8.7−6.8 (br, *Ar*), 3.2−1.6 (br, *aliphatic*). ^{13}C{^{1}H} NMR (THF-d_8): δ 146.3, 129.9, 126.1, 114.7, 46.4, 41.3, 35.6. ^{19}F{^{1}H} NMR (THF-d_8) (ppm): −62.41 (br). IR (KBr, cm^{-1}): 2931, 2860, 1713, 1619, 1461, 1377, 1284, 1148, 961, 895, 840.

Synthesis of *alt*-6−CO Copolymer. The procedure was analogous to that of **1**−CO copolymer, except only 4 mL of solvent was used. White powdery solid was yielded (41%). Anal. Calcd for $(C_{10}H_5F_5O)_n$: 50.9% C, 2.1% H, 40.2% F. Found: 51.0% C, 2.1% H, 40.5% F. ^{1}H NMR ($CDCl_3$) (ppm): 3.10 (br, 1H, benzylic C*H*$_2$), 2.76 (br, 1H, backbone C*H*), 2.56 (br, 2H, backbone C*H*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$) (ppm): 211.6 (*C*=O), 145.3 (d, Ar_{CF}, $^1J_{CF}$ = 247.0 Hz), 140.5 (d, Ar_{CF}, $^1J_{CF}$ = 253.5 Hz), 137.9 (d, Ar_{CF}, $^1J_{CF}$ = 252.2 Hz), 111.2 (Ar_{ipso}), 46.9−43.8 (br, backbone *C*H$_2$ and *C*H), 24.1 (benzylic *C*H$_2$). ^{19}F{^{1}H} NMR ($CDCl_3$) (ppm): −139.8 (br, C−F_{meta}), −153.2 (br, C−F_{para}), −154.9 (br, C−F_{ortho}). IR (KBr, cm^{-1}): 2938, 2642, 1713, 1655, 1519, 1496, 1343, 1120, 1055, 945, 832, 750.

Water Contact Angle Measurements of Polymer Blends. Appropriate amounts of fluorinated copolymer, poly-

styrene, and/or poly(methyl methacrylate) were combined and dissolved in $CHCl_3$ or THF. The solution was then spin-coated onto a glass slide, which was allowed to dry. Water drops were dropped onto the slide with a precision micrometer syringe. Contact angles were measured on either side of at least three drops and averaged.

Conclusions

Six alternating copolymers of fluorinated allylbenzene derivatives with carbon monoxide were synthesized and characterized. The allylpentafluorobenzene−carbon monoxide copolymer (**6**−CO copolymer), when blended in small amounts with poly(methyl methacrylate) (PMMA), significantly increased the water contact angle of PMMA. Spectroscopic data indicate the that **6**−CO is the only copolymer that is pure 1,4-polyketone, whereas the other copolymers contain significant quantities of spiroketal runs in the polymer backbone. Keto groups, but not spiroketal, are proposed to engage in nonbonding interactions with the polar groups of PMMA, thus orienting the fluorinated pendant group toward the film surface, resulting in unusually high hydrophobicity of the surface.

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