Table I. Polymerization of *p*-**3** and *m*-**3** by $TaCl_5$–Cocatalyst Systems[a]

cocatalyst	monomer conversn, %	polymer[b] yield, %	$\bar{M}_w$,[c] 10^5	$\bar{M}_n$,[c] 10^5
		p-**3**		
n-Bu_4Sn	95	85	22	7.5
Et_3SiH	100	71	21	5.7
		m-**3**		
n-Bu_4Sn	100	87	14	2.5
Et_3SiH	100	93	10	2.1

[a] Polymerized in toluene at 80 °C for 2 h; $[M]_0$ = 0.50 M, $[TaCl_5]$ = 20 mM, concentration of cocatalyst = 40 mM. [b] Methanol-insoluble product. [c] Determined by GPC.[10]

Table II. Gas Permeability of Silicon-Containing Polymers

polymer	P^a He	H_2	O_2	N_2	CO_2	CH_4	P_{O_2}/P_{N_2}
poly(*p*-**3**)	1000	2100	1100	520	4700	1500	2.1
poly(*m*-**3**)	1000	2100	1200	610	4000	1500	2.0
poly(**1**)	3300	7800	4500	2700	29000	6500	1.7
PDMS[b]	230	460	490	230	3200		2.1

[a] Gas permeability coefficients at 25 °C in the units of 1×10^{-10} $cm^3(STP)\cdot cm/(cm^2\cdot s\cdot cmHg)$ (=barrer). [b] At 0 °C; from ref 17c.

absorptions only below 500 nm,[12] indicating that conjugation of the main chain is relatively short. Free-standing films could be obtained by casting the polymers from toluene solution. The temperatures at which weight loss starts in TGA (in air, heating rate 10 °C/min) were 420 and 400 °C for poly(*p*-**3**) and poly(*m*-**3**), respectively; these values are somewhat lower than that for poly(**2**), but fairly higher than those for any other substituted polyacetylenes.[9c] No decrease in molecular weight was observed even though the present polymers were heated in air at 120 °C for 20 h. Thus, it can be said that these polymers have excellent thermal stability. The polymers were hard and brittle with respect to mechanical properties.[13] Their glass transition temperatures measured by dynamic viscoelasticity were above 200 °C.[14]

The oxygen permeability coefficients,[15] P_{O_2}, of poly(*p*-**3**) and poly(*m*-**3**), were about twice the value of poly(dimethylsiloxane) (PDMS), which is well-known as a highly gas-permeable rubber, and about a quarter the value of poly(**1**), which is the most permeable to oxygen (Table II).[16,18] The permeability coefficients of the present polymers to other gases are also $^1/_3$–$^1/_7$ those of poly(**1**); thus the permeation behaviors of these three polymers are similar. The P_{O_2}/P_{N_2} values of the present polymers are larger than that of poly(**1**) and similar to that of PDMS, corresponding to a general tendency that the lower the permeability of a polymer, the higher the permselectivity of the polymer. It is noteworthy that the present polymers show high gas permeability, although aromatic polymers are generally the least gas permeable among substituted polyacetylenes [e.g., poly(1-phenyl-1-propyne); P_{O_2} = 6.3 barrer[1d]].

Acknowledgment. We thank Dr. Y. Hirokawa for cooperation in gas-permeability measurements. This research was partly supported by a grant-in-aid from the Ministry of Education, Japan (No. 02205068).

Registry No. **1** (homopolymer), 87842-32-8; *p*-**3** (homopolymer), 136459-73-9; *m*-**3** (homopolymer), 136459-75-1; He, 7440-59-7; H_2, 1333-74-0; O_2, 7782-44-7; N_2, 7727-37-9; CO_2, 124-38-9; CH_4, 74-82-8; $TaCl_5$, 7721-01-9; *n*-Bu_4Sn, 1461-25-2; Et_3SiH, 617-86-7.

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[11] Poly(*p*-**3**): ^1H NMR ($CDCl_3$, 270 MHz) δ 7.5–5.5 (br s, 9, Ph), –0.5 (br s, 9, $SiMe_3$); IR (KBr) 2990 (s), 1650 (w), 1600 (m), 1500 (m), 1440 (m), 1250 (s), 1120 (s), 840 (s), 810 (w), 750 (m), 700 (m), 630 (m), 550 (s) cm^{-1}. Anal. Calcd for $(C_{17}H_{18}Si)_n$: C, 81.5; H, 7.2; Si, 11.2. Found: C, 81.9; H, 7.0. Poly(*m*-**3**): ^1H NMR ($CDCl_3$, 270 MHz) δ 7.5–5.5 (br s, 9, Ph), –0.5 (br s, 9, $SiMe_3$); IR (KBr) 2990 (s), 1600 (m), 1500 (m), 1440 (m), 1250 (s), 1120 (s), 840 (s), 780 (m), 750 (m), 700 (m), 630 (m), 570 (m) cm^{-1}. Anal. Found: C, 81.1; H, 7.7.

[12] UV_{max} (THF): poly(*p*-**3**), 430 nm (ε 5000); poly(*m*-**3**), 425 nm (ε 4800).

[13] The tensile properties at 25 °C were as follows. Poly(*p*-**3**): Young's modulus (E), 1460 MPa; elongation at break (γ_B), 1.5%; tensile strength (σ_B), 19 MPa. Poly(*m*-**3**): E, 800 MPa; γ_B, 2.1%; σ_B, 14 MPa.

[14] Dynamic mechanical measurements were performed with a Rheovibron Model DDV-II-C instrument (Toyo Baldwin Co.).

[15] Gas permeability coefficients were measured with a K-315-N gas permeability apparatus (Rikaseiki Co.).

[16] The absolute P_{O_2} values of highly gas permeable, glassy polymers vary widely. Their relative values are as follows (25 °C): poly(TMSP), 1.0; poly(MeC≡CGeMe$_3$), 0.40;[17a] poly(MeC≡CSiEt$_3$), 0.20;[17b] poly(MeC≡CSiMe$_2$Et), 0.11;[1b] cf. PDMS 0.10.[17c]

[17] (a) Langsam, M. U.S. Patent 4 759 776, 1988. (b) Masuda, T.; Isobe, E.; Hamano, T.; Higashimura, T. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1353–1362. (c) Pauly, S. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; pp VI/435–449.

[18] According to a preliminary experiment, the P_{O_2} values after the aging of polymers at 80 °C for 26 h in vacuum were as follows: poly(*p*-**3**), 600 barrer (P_{O_2}/P_{N_2} = 2.0); poly(*m*-**3**), 67 barrer (P_{O_2}/P_{N_2} = 2.9); poly(**1**), 330 barrer (P_{O_2}/P_{N_2} = 2.6). Thus, quite interestingly, the P_{O_2} value of poly(*p*-**3**) was much less affected by time, temperature, and pressure.

Observation of an Unusual Surface Reaction: Direct Abstraction of CO from Furan Adsorbed on Molybdenum Surfaces

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The catalyzed removal of heteroatoms from heterocycles is an important part of the processing of petroleum and coal to liquid fuels. The surface chemistry of thiophene adsorbed on single-crystal model catalysts has received some considerable attention.[1-3] No corresponding studies involving the O analogue, furan, have been reported; there have been experiments conducted at high pressures.[4] During preliminary experiments on this system we have noted an unusual mode of surface reaction that distinguishes furan from thiophene. Thiophene decomposes to atomic fragments on such surfaces, and the only gas-phase product is dihydrogen. The S heteroatom remains firmly bonded to the Mo surface. In the case of furan we observe the *low-temperature direct abstraction of the heteroatom from the furan molecule to form a stable gas-phase reaction product*: *carbon monoxide*. The reaction occurs on both the (100) and (110) surfaces of molybdenum, both clean and when sulfur overlayers are present.

The experiments have been performed in a standard vacuum system containing facilities for low-energy electron diffraction and Auger electron spectroscopy. Sulfur overlayers were deposited from a solid-state electrochemical source, and furan was admitted from a doser with the crystal at 225 K. Temperature-programmed reaction spectroscopy (TPRS) was then used to monitor the fate of adsorbed furan.

The TPRS spectrum from a saturation furan dose (about 0.5 L) on a Mo(100) surface with approximately 0.2 ML of adsorbed sulfur (Figure 1) reveals significant signals at m/e values of 68, 39, 28, and 2. The 39 and 68 amu desorption signals apparent near 275 K are the dominant cracking fraction and parent peaks from molecularly adsorbed furan. The 2 amu signal is similar to reports[3,5] of the H_2 TPRS spectrum from thiophene/Mo(100) and can be reasonably assigned to stepwise dehydrogenation of chemisorbed hydrocarbon intermediates after dissociative adsorption of furan. The 28 amu spectrum shows a low-temperature peak at about 330 K followed by two small peaks and a further peak that commences below 1000 K and continues to above 1100 K. A fragment of m/e 28 is not a significant cracking feature of the mass spectrum of furan, and furthermore, the low-tem-

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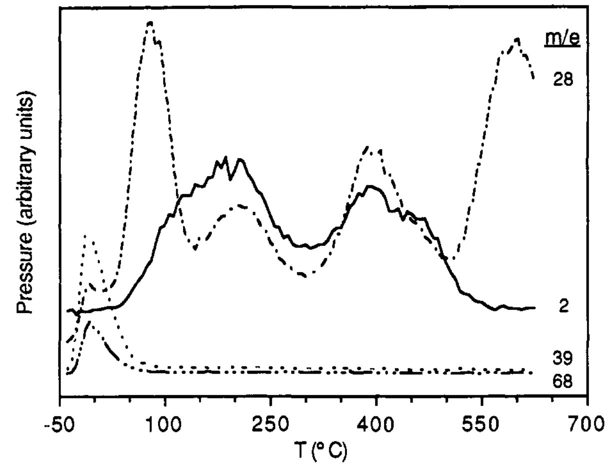


Figure 1. Temperature-programmed reaction spectra resulting from the adsorption of a saturation dose of furan on partially sulfided Mo(100) (Θ_S = 0.2 ML), showing the signals corresponding to m/e = 2 (dihydrogen), 28 (carbon monoxide) and 39 and 69 (furan). Adsorption took place at 273 K, and the heating rate was 10 K/s. The partial pressures were uncorrected for differences in ionization efficiency and transmission in the mass spectrometer.

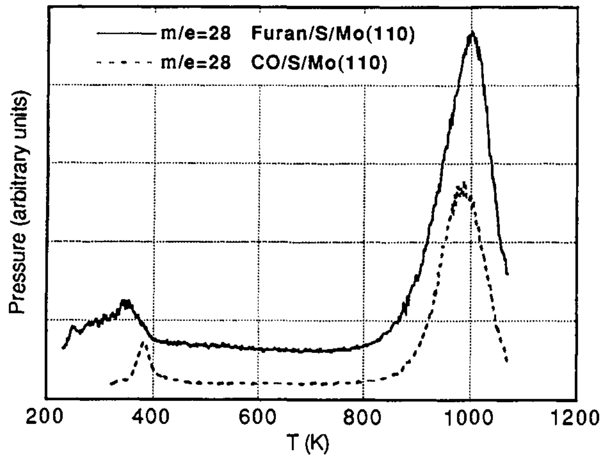
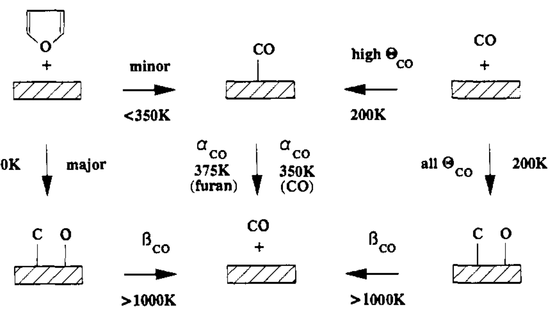


Figure 2. Temperature-programmed reaction spectra for m/e = 28 resulting from the adsorption of furan and CO on partially sulfided Mo(100) (Θ_S = 0.2 ML) under the same conditions as Figure 1.

perature 28 amu desorption peak commences at a temperature at which all of the molecularly adsorbed furan has already desorbed. Hence this 28 amu signal most probably arises from the production of carbon monoxide or ethylene on the surface. A careful examination of masses corresponding to all of the possible cracking products from these materials showed that this entire spectrum is in fact attributable to CO desorption from adsorbed furan.

The 28 amu TPRS data for the CO/Mo(110) spectrum shown in Figure 2 contains two peaks. The low-temperature peak only appears at high coverages of CO and is attributed to first-order desorption of molecularly bound α-CO. The high-temperature β peak is interpreted as a recombination of C and O atoms from dissociated CO.[6,7] The 28 amu trace for furan/Mo also exhibits these two features at desorption temperatures very similar to those observed for adsorbed CO. The similarity of the major 28 amu peaks from furan adsorption to those seen from CO adsorption leads us to the conclusion that, while a substantial amount of furan does indeed decompose to give atomic carbon and oxygen on the surface, which later desorbs as β-CO, a direct CO abstraction route also occurs at low temperatures close to 350 K. The CO released from the furan molecule during this process is then immediately desorbed, as it is above the normal α-CO desorption temperature (Scheme I).

Scheme I



We find support for this type of reaction chemistry in gas-phase pyrolysis experiments.[8] Here it is found that ring-opening of furan to form a stabilized biradical that subsequently decomposes into propyne and CO is a favored low-energy reaction pathway. Such a mechanism may apply here to furan that has become bonded to the surface through loss of an α-H. There are also parallels with the complex reported by Vollhardt[9] in which a THF-like species is α-C bonded to Mo as a Fischer carbene, which decomposes to propene and a CO ligand bonded to the Mo.

This low-temperature direct abstraction of CO from furan, though a minority reaction on these surfaces, stands in contrast to the complete retention of sulfur from thiophene on the same surface. Though a surprising reaction at first sight, in hindsight the possibility of forming a stable gas-phase product in the case of furan, but not in the case of thiophene, provides an obvious driving force for this differing behavior.

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Real-Time Analysis of Chemical Reactions Occurring at a Surface-Confined Organic Monolayer

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We report the first real-time measurements of a chemical reaction between a surface-confined organic monolayer and a vapor-phase reactant.[1] To demonstrate monolayer reaction

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(1) Surface reactions similar to those reported here have been previously carried out in solution by, first, Sagiv and, in elegant recent examples, Mallouk, Ulman, Whitesides, and Marks and Ratner. See: (a) Pomerantz, M.; Segmuller, A.; Netzer, L.; Sagiv, J. *Thin Solid Films* **1985**, *132*, 153. (b) Gun, J.; Iscovici, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *101*, 201. (c) Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* **1983**, *100*, 67. (d) Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* **1983**, *99*, 235. (e) Lee, H.; Kepley, L. J.; Hong, H.-G.; Mallouk, T. E. *J. Am. Chem. Soc.* **1988**, *110*, 618. (f) Ulman, A.; Tillman, N. *Langmuir* **1989**, *5*, 1418. (g) Ulman, A. *J. Mater. Educ.* **1989**, *11*, 205. (h) Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir* **1989**, *5*, 101. (i) Wasserman, S. R.; Whitesides, G. M.; Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Axe, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5852. (j) Li, D.; Ratner, M. A.; Marks, T. *J. Am. Chem. Soc.* **1990**, *112*, 7389.

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