M $NaHSO_3$ (or metabisulphite), dried ($MgSO_4$), and concentrated. Distillation at 52 °C (29 mm) afforded 1.57 g (55%) of cyclohexene oxide. A reduction in the amount of H_2O_2 and buffer by as much as one-half did not have a deleterious effect on the yields. The use of either ethyl ether or toluene as solvent resulted in a substantial reduction in yield.

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Registry No. 6, 70288-43-6; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; norbornene, 498-66-8; cyclooctene, 931-88-4; 1-nonene, 124-11-8; cyclohexene epoxide, 286-20-4; 1-methylcyclohexene epoxide, 1713-33-3; norbornene epoxide, 278-74-0; cyclooctene epoxide, 286-62-4; 1-nonene epoxide, 28114-20-7; 2-methylcyclohexanone, 583-60-8; H_2O_2, 7722-84-1; ethyl chloroformate, 541-41-3.

Synthesis and Thermal Solid-State Polymerization of a New Diacetylene: 2,4-Hexadiynylene Bis(*p*-fluorobenzenesulfonate)

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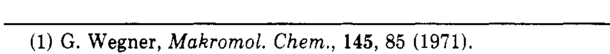
Of all the diacetylenes (RC≡C–C≡CR) reported to date, PTS (R = *p*-$CH_3C_6H_4SO_3CH_2$)[1] is the most investigated system. PTS monomer has been used as a model compound to study the kinetics and mechanism[2-6] of solid-state polymerization of diacetylenes. The resulting PTS polymer has also been used as a prototype for studying the electrooptical properties[7-20] of a pseudo-one-dimensional organic polymer. Thus far, no large single crystals of diacetylene sulfonates isomorphous with PTS have been available for a comparative investigation. It has been shown that the solid-state reactivity of diacetylene monomers is governed by their spatial arrangement in the crystal lattice as well as by their functional groups.[21] A closely related compound, 2,4-hexadiynylene bis(*p*-chlorobenzenesulfonate), has recently been reported to be inactive in the solid state.[22]

The most interesting induction period followed by an autocatalytic behavior observed in the thermal polymerization of PTS has been attributed[2,23] to the large mismatch (~5%) between monomer and polymer repeat units along the chain direction. Our recent findings on the solid-state polymerization of DCHD (R = $CH_2N(C_6H_4)_2$)[24] which shows an S-shaped conversion–time curve upon thermal or γ-ray polymerization have provided supporting evidence that the autocatalytic effect in PTS is due to an increase in chain propagation length. Theoretically, the autocatalytic effect in PTS has been related to the strain energy associated with the monomer–polymer solid solution by Baughman's model.[25] However, any direct comparison between PTS and DCHD must be regarded with caution since they differ in functional groups. This paper reports on the synthesis and solid-state thermal polymerization of the new diacetylene 2,4-hexadiynylene bis(*p*-fluorobenzenesulfonate) (hereafter referred to as PFBS). The structure of the monomer is



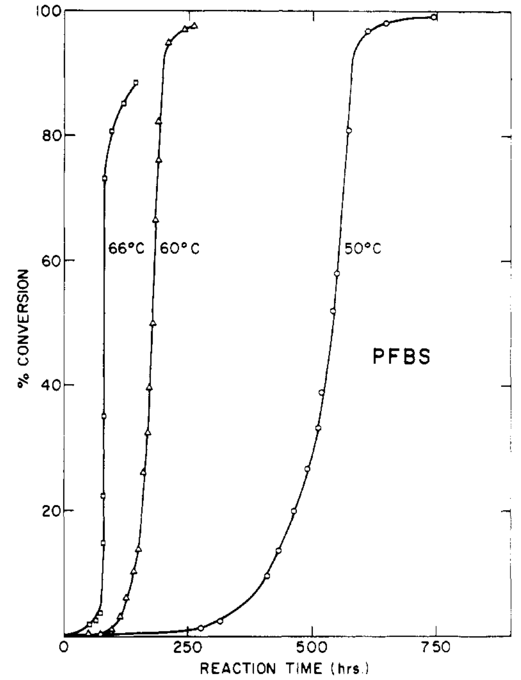


Figure 1. Thermal polymerization of PFBS at 50, 60, and 66 °C. Percent conversion is determined as the insoluble polymer fraction after extraction with acetone at room temperature.

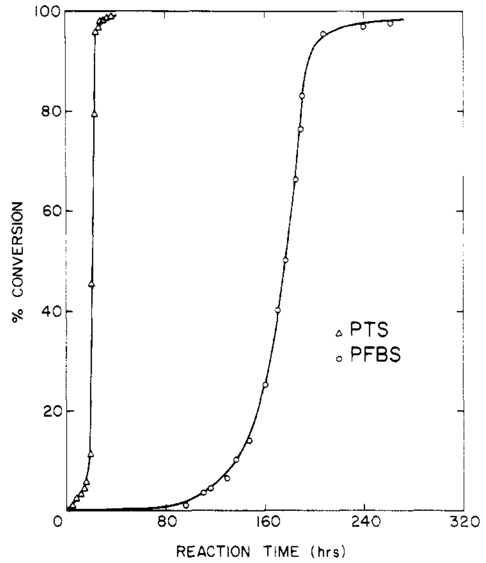


Figure 2. Time–conversion curves for PTS and PFBS at 60 °C. Data for PTS are from ref 23.

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Thermal Polymerization of PFBS

The newly synthesized diacetylene PFBS was found to have an apparent induction period accompanied with an autocatalytic effect upon thermal polymerization. The results of thermal polymerization are shown in Figure 1. Like PTS, the diacetylene PFBS shows dramatic color changes from red to a metallic gold color as the thermal polymerization proceeds. The rate of thermal polymerization was found to be significantly slower than that of the PTS system. The results of the kinetics at 60 °C showed that the rate of polymerization for PFBS was about 1 order of magnitude lower than that of PTS (see Figure 2). Calculations show that the activation energy (E_a) for the thermal polymerization of PFBS is 26 kcal/mol. This can be compared to the E_a for PTS,[2,3] 22 kcal/mol.

The difference between the thermal reactivities of PFBS and PTS in the solid state can be explained by a mechanical-strain model developed by Baughman.[25] X-ray diffraction studies show that the repeat dimension (*b* axis) of the PFBS monomer in the reaction direction is 5.18 Å. Upon complete polymerization, this dimension was reduced to 4.90 Å. This corresponds to a 5.4% change in the reaction direction. For comparison, in the PTS system the change along the reaction direction upon thermal polymerization is about 4.7% (from 5.15 to 4.91 Å). Apparently, the change along the reaction direction in the PFBS system is larger than that in the PTS system. Consequently, PFBS has a longer induction period for polymerization and the reactivity of PFBS is lower than that of PTS.

We have found that the crystals (obtained by crystallization from common organic solvents) of 2,4-hexadiynylene bis(*p*-bromobenzenesulfonate) are not solid-state polymerizable. If the solid-state polymerizability is governed by the steric effect alone, the bromo-substituted benzenesulfonate should at least be reactive, since the effective size of the Br group (1.95) is approximately the same as the CH_3 group (2.0) as indicated by their van der Waals radii.[26] The nonreactivity could be attributed to the formation of donor–acceptor complexes between the substituents since the Br group is known to form a complex with the aryl ring.[27] Recently, X-ray crystal structure analyses have shown that the nonreactivity of the needle crystals (CH_2Cl_2/hexane) of 2,4-hexadiynylene bis(*p*-chlorobenzenesulfonate) is due to the nonbonded chlorine–phenyl interaction, which modifies the monomer's lattice packing so as to result in an inactive phase.[22] It appears that PFBS is the first modified diacetylenylene bis(arylsulfonate) which polymerized in the solid state in analogy to PTS. It is conceivable that the solid-state polymerizability of PFBS has something to do with the F atom's electronegativity.[28] It has been shown that the p-donor property of the F radical is significantly lower than that of the Cl radical.[29] Consequently, the F atoms' lone pair electrons in PFBS would not complex with the aryl ring, and hence the PFBS monomers can polymerize accordingly in analogy to the PTS system.

Table I. Comparison of Lattice Parameters of PFBS and PTS

	PFBS		PTS	
	monomer	polymer	monomer[a]	polymer[b]
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	13.94	13.93	14.60	14.49
b, Å	5.18	4.90	5.15	4.91
c, Å	14.09	14.06	15.02	14.94
β, deg	114.1	113.3	118.4	118.1
Z	2	2/*n*	2	2/*n*
M_r	426.4	*n*(426.4)	418.5	*n*(418.5)

[a] Data from ref 23. [b] Data from D. Kobelt and E. F. Paulus, *Acta Crystallogr., Sect. B*, **30**, 232 (1974).

It has been shown that PTS polymer undergoes a doubling of the unit cell along the *c*-axis direction[30] accompanied with a doubling of the electronic absorption spectrum[13,17,31] as the temperature is lowered from 300 to 200 K. Thus far, no other diacetylene polymer has been reported to exhibit such a phase-transition phenomenon. The availability of large single crystals for PFBS polymer thus provides a unique opportunity for further investigating and understanding the electrooptical properties of poly(diacetylenes) (preliminary investigations show that PFBS polymer crystals do not show a "doubling" of the electronic absorption spectrum as the temperature is lowered from 300 to 4 K).[32]

The newly synthesized PFBS also shows an induction period accompanied with autocatalytic behavior upon γ-ray polymerization. In addition, we have found that certain fluorinated benzenesulfonate diacetylene compositions, such as diacetylene bis(*m*-(trifluoromethyl)benzenesulfonates), are also capable of undergoing solid-state polymerization. Preliminary investigations show that PFBS cocrystallizes with isomorphous diacetylene PTS. The resulting solid solutions retain their parent compounds' autocatalytic behavior upon thermal copolymerization but have different apparent induction periods as the molar ratios change. The details will be reported in a full paper.

Experimental Section

The diacetylene monomer PFBS is synthesized in high yield by reacting *p*-fluorobenzenesulfonyl chloride with 2,4-hexadiyne-1,6-diol according to the method of Wegner[1] with slight modifications. The crude product was purified by liquid column chromatography with silica gel, giving rise to very light yellow

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crystals (mp 70–71 °C) which turn pink upon light exposure. Elemental analysis was satisfactory. Anal. Calcd for $C_{18}H_{12}O_6F_2S_2$: C, 50.70; H, 2.84. Found: C, 50.41; H, 2.88. Crystallizations from various common organic solvents gave crystals of different morphological structures (hexagon, diamond, or platelike). Large platelike single crystals with dimensions of 0.3 × 2 × 10 mm^3 can be obtained from a 10% (v/v) acetone/petroleum ether solution by slow evaporation.

The PFBS crystals can be polymerized quantitatively by γ irradiation or by thermal annealing. The resulting PFBS polymer crystals, which are infusible and insoluble in common organic solvents, have practically the same shape as the monomer crystals and are metallic gold in color. Like PTS, the PFBS polymer crystals are strongly dichroic, with the axis of dichroism parallel to a rapid growth direction of the monomer phase. The PFBS polymer crystals were shown to have the correct structure as evidenced from IR and Raman spectroscopy [ν(C=C) 1485, 1464 cm^{-1} (shoulder); ν(C≡C) 2087 cm^{-1}] and elemental analysis. Anal. Calcd for $(C_{18}H_{12}O_6F_2S_2)_n$: C, 50.70; H, 2.84. Found: C, 50.42; H, 2.92. X-ray diffraction studies show that PFBS polymer crystals are monoclinic with space group $P2_1/c$ (Table I). The repeat unit along the polymer chain (*b* axis) is 4.9 Å. Assuming there are two monomer units per unit cell, the calculated density for the polymer is 1.605 g/cm^3, in good agreement with the measured bulk density (1.60 g/cm^3). These results are consistent with the polymerization of PFBS monomer crystals by a 1,4-addition reaction, in analogy to the PTS system.

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Registry No. PFBS, 70287-75-1; PFBS polymer, 70287-76-2; 2,4-hexadiyne-1,6-diol, 3031-68-3.

Homogeneous Catalytic Activation of Carbon-Hydrogen Bonds. Hydrogen-Deuterium Exchange in Saturated Carboxylic Acids[1]

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Certain soluble transition-metal complexes are known to activate the carbon-hydrogen (C–H) bonds of hydrocarbons.[3-5] Evidence of this bond activation through transition-metal complexation is demonstrated by the simple reaction wherein hydrogen is exchanged by deuterium. Successful hydrogen-deuterium (H–D) exchange reactions have been reported on numerous aromatic compounds,[6,7] and a number of saturated and unsaturated hydrocarbons.[8-11] To date, however, only a few reports have appeared on the transition-metal activation of the C–H bonds found in functionally substituted alkanes.[12-15] Our interest in preparing functionally substituted fatty acids prompted us to extend the scope of this reaction to include simple saturated carboxylic acids.

Table I. Exchange of Hydrogen for Deuterium in Methyl Nonanoate Catalyzed by K_2PtCl_4[a]

expt no.	[C_9 acid], M	time, h	av no. of ^2H/ molecule	% D(MS)[f]
1	0.2	20	1.96	9.8 (46.7)
2	0.2	65	5.32	26.6 (46.3)
3	0.2	102.5	6.82	34.1 (42.0)
4	0.2[b]	139	5.86	29.3 (47.5)
5	2.0	96	2.62	13.1 (33.7)
6	2.0[c]	96	2.38	11.9 (34.3)
7	2.0[d]	96	2.96	14.8 (34.4)
8	2.0[e]	47.5	1.60	8.0 (35.7)

[a] $[PtCl_4]^{2-}$ = 0.04 M for all experiments. Catalyst remained homogeneous throughout the experiment. [b] $[PtCl_6]^{2-}$ used instead of Pt(II) salt. Catalyst remained homogeneous throughout the experiment. [c] 3 mmol of $HClO_4$. [d] Open-flask system. [e] 6 mmol of H_2SO_4-*d*. [f] % D determined by mass spectrometry. Value in parentheses is theoretical % ^2H expected at equilibrium, based on actual reaction concentration.

Initial experiments were carried out with nonanoic acid as our model compound with subsequent reactions carried out on decane and branched carboxylic acids. The reaction conditions were essentially those described by Hodges et al.[9] The reactions were carried out on the carboxylic acid or decane in sealed ampules, heated at 100 °C. The catalytically deuterated samples, after esterification, were analyzed by mass spectrometry to ascertain the total percent ^2H incorporated and by ^2H NMR to determine the site of bond activation. We found that changes in various reaction parameters affected the extent and rate of the H–D exchange reaction. These trends are outlined in Table I. As anticipated, with increased reaction times (20–102 h, experiments 1–3), ^2H incorporation increased. Similarly, larger catalyst/acid ratios (experiments 3 and 5, Table I) yielded larger ^2H incorporations. Nevertheless, theoretical equilibrium concentrations of ^2H were never achieved. The values in parentheses (Table I) denote the amount of ^2H to be expected if all the ^2H and hydrogen in the reaction medium were equilibrated. At increased reaction time, the average ^2H content per molecule increased. With an increased level of ^2H incorporation, the Pt metal is statistically more likely to encounter and cleave a C–D bond over a C–H bond thus making it difficult to reach theoretical equilibrium. The presence of polydeuterated species may be accounted for by this equilibrium process. An alternative explanation for the polydeuterated species may be that dimeric complexes of Pt are responsible for multiple exchanges.[9]

We also found, as have others,[9] that the presence of pyrene and the acidity of the reaction medium are important for keeping the catalyst homogeneous throughout the reaction. The aromatic compound and a mineral acid presumably suppress the disproportionation of the Pt(II) ion to Pt(0).[9] Increased concentrations of pyrene and/or $HClO_4$ (experiment 6, Table I) had essentially no effect on the H–D exchange reaction. We did find, however, that

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