Kinetics of polymer surface fluorination: Elemental and plasma-enhanced reactions

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E.s.c.a. spectra of surface fluorinated polyethylene, poly(vinyl fluoride), and poly(vinylidene fluoride) are reported. Two reaction environments were used in this study: exposure to elemental fluorine and immersion in a glow discharge plasma. The systematic variation of fluorine composition in the polymer phase is shown to have a dramatic effect on the kinetics of the elemental reaction and little effect in the plasma reaction.

Keywords Polymer reaction; kinetics; fluorine chemistry; surface modification; plasma reaction; glow discharge reaction

INTRODUCTION

The fluorination of organic compounds with elemental fluorine gas exhibits unusual kinetics. At low conversions (with respect to a perfluorinated product), fluorine is an aggressive reactant; as conversion increases, the deactivation effect of substituent fluorine dominates and slows the reaction rate[1]. Similar results have been observed with the surface fluorination of polyethylene exposed to fluorine gas[2]. Polymer fluorination was carried out in a glow discharge plasma in an attempt to surmount the deactivation problem[3,4]. The relative success of the glow discharge reaction environment is examined in more detail in this work. Polyethylene (PE), poly(vinyl fluoride) (PVF), and poly(vinylidene fluoride) (PVF_2) were the model polymers chosen for this study. Experiments focused on what effect the controlled addition of fluorine to the polyethylene chain has on the kinetics of the elemental and plasma reactions. X-ray photoelectron spectroscopy (e.s.c.a.) data are reported for the polymer reactants and products. The kinetic results are discussed in light of other organic fluorination data and proposed reaction mechanisms.

EXPERIMENTAL

The low-density polyethylene film used in these experiments was supplied by the Dow Chemical Company (PE-303). Elemental surface analysis of the film, determined by e.s.c.a., revealed the presence of a small amount of oxygen. The poly(vinyl fluoride) was supplied as powder from the Scientific Polymer Products Corporation and was solvent cast from *N*,*N*-dimethylformamide. A small oxygen signal was again present in the e.s.c.a. spectra of the PVF films. The poly(vinylidene fluoride) was also purchased from Scientific Polymer Products and was solvent cast from dioxane. This film surface was devoid of any oxygen species. The oxygen present in the PE and PVF films is insignificant with respect to the general observations and conclusions of this work.

A premixture of 5% fluorine gas diluted with argon was used as received from the Matheson Company.

The quartz flow reactor used for both elemental and plasma reactions is identical to the one reported by Anand *et al.*[3,4]. The power was supplied by an LFE Corporation rf generator (13.56 MHz) inductively coupled to the reactor. For elemental reactions, the polymer was placed in the reactor, the vessel was evacuated with a mechanical vacuum pump, and the fluorine/argon reaction gas was metered in. The plasma reactions were similar except that power was supplied to the induction coils to strike a glow. Typical operating conditions were: Pressure—267 Pa (2 torr); Power (rf)—50 watts; Flow Rate—50 cm^3 (STP)/min.

E.s.c.a. was the surface sensitive analytical technique used in this study to characterize the polymer surfaces[5]. The information that we extracted from this technique included quantitative elemental analysis (carbon, fluorine, and oxygen) and qualitative analysis of the carbon molecular environments through carbon 1s chemical shifts. A Physical Electronics (Model 548) spectrometer was used to acquire the e.s.c.a. spectra.

RESULTS AND DISCUSSION

Carbon $_{1s}$ e.s.c.a. spectra of untreated and reacted polymers are presented in *Figure 1* for PE, *Figure 2* for PVF and *Figure 3* for PVF_2. Energy referencing was achieved by assigning the $-CH_2-$ structural feature to 285 eV, regardless of beta substituent groups. This policy allows for direct (vertical) comparison of the primary spectral features: $-CH_2-$ ($=285$ eV), $-CHF-$ ($\simeq 287.5$ eV) and $-CF_2-$ ($\simeq 290$ eV). Elemental compositions and F/C molar ratios were determined from atomic sensitivity factors and integrated peak areas[6].

The elemental fluorination reactions exhibit the dual behaviour of fluorine, as a reactive gaseous species and as a deactivating substituent atom. With polyethylene, partial fluorination is observed early in the reaction, but the rate of fluorination then slows considerably. This rate may be accelerated by increasing the fluorine partial pressure, but the selectivity problem still persists. Similar effects are observed with PVF. In the case of PVF_2, the overall reaction rate essentially drops to zero. In no case was the F/C ratio of the reaction product greater than 1. While it is not possible to deconvolute the intrinsic gas-solid reaction kinetics from the e.s.c.a. spectra, qualitative trends are evident. In the context of the proposed free radical chain reaction mechanism[1], the intrinsic rate constant for abstracting a $-CHF-$ proton is much less

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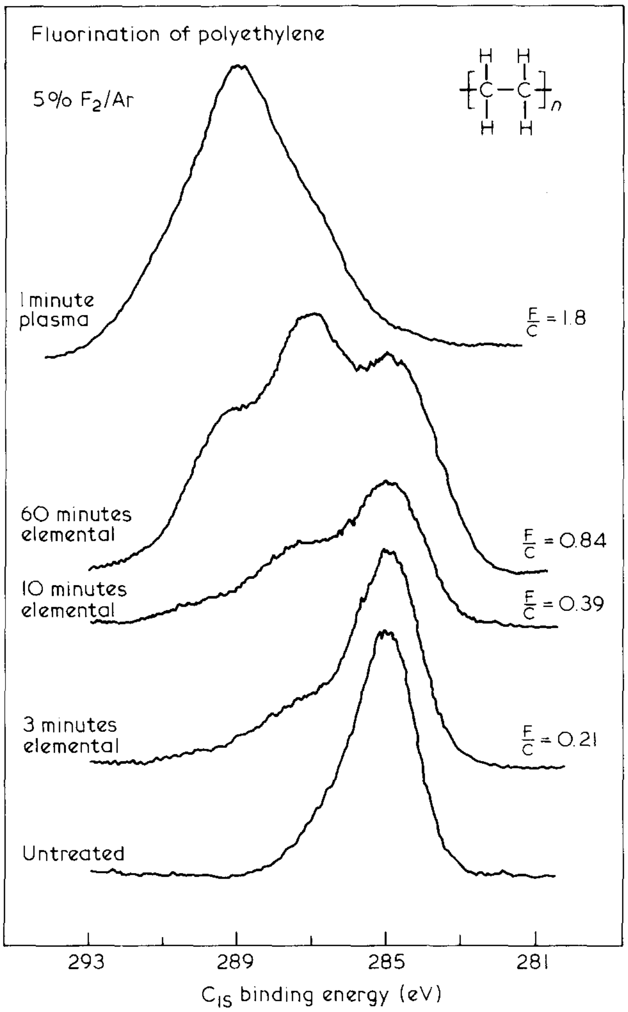

Figure 1 C_{1s} e.s.c.a. spectra of untreated and reacted polyethylene film

than that of a $-CH_2-$proton. The experimental data suggest that perfluorination of any polymer with elemental fluorine will necessarily be slow due to the strong deactivation effect of substituent fluorine.

In the plasma experiments, fluorine exhibits its reactive nature. The relative success of this reaction environment is evident from the carbon 1s e.s.c.a. spectra. Regardless of the fluorine content of the initial polymer, rapid fluorination within the e.s.c.a. sampling depth (~ 50 Å) is achieved in less than 1 minute reaction time. The structure of the C_{1s} peak is not identical to PTFE[3]. This may be due to unreacted $-CH_2-$ groups at the deeper end of the e.s.c.a. sampling region, $-\overset{|}{\underset{|}{C}}F$ and $-CF_3$ groups resulting from main chain cleavage, partially reacted $-CHF-$ groups, and beta chemical shifts broadening the $-CF_2-$ peak. With respect to the top monolayer of these plasma reacted polymers, contact angle measurements indicate low energy (hydrophobic) surfaces characteristic of perfluorinated polymers.

The observed kinetic trends in the elemental experiments are consistent with the polyethylene experiments of Clark *et al.*[2] and the poly(vinyl fluoride) work reported by Shinohara *et al.*[7]. They also conform qualitatively with non-polymeric organic fluorination reactions. Tedder[8] reports that elemental fluorination is relatively unselective with respect to primary, secondary, and tertiary hydrogen atoms of unsubstituted hydrocarbons due to the extremely reactive nature of fluorine. However, in the gas phase fluorination of 1-fluorobutane[9] the alpha and beta carbons were shown to be deactivated. This was explained by the adverse polar effect of substituent fluorine on the C–H–F transition state, which should lead to an increase in the activation energy of the proton abstraction reaction. Another theory which has been proposed[1] is that fluorine substituent atoms reduce the reaction rate due to steric hindrance. The elemental fluorination data are consistent with a free radical chain reaction mechanism in which the initiation step limits the kinetic rate as the reaction progresses.

The experimental results in the plasma environment are in accord with published data on polyethylene fluorination[3,4]. The plasma enhanced reactions may avoid the fluorine deactivation effect *via* the interaction of 'reactive' plasma species with the polymer to generate radicals in the polymer phase. These species include photons, electrons, ground state and excited atoms, molecules, radicals and ions. Another possibility is that the proton abstraction rate may be significantly increased due to the relatively high atomic fluorine concentration, the steady state value in the glow being orders of magnitude larger than the equilibrium value. The relative importance of these plasma species in accelerating the reaction kinetics is not known.

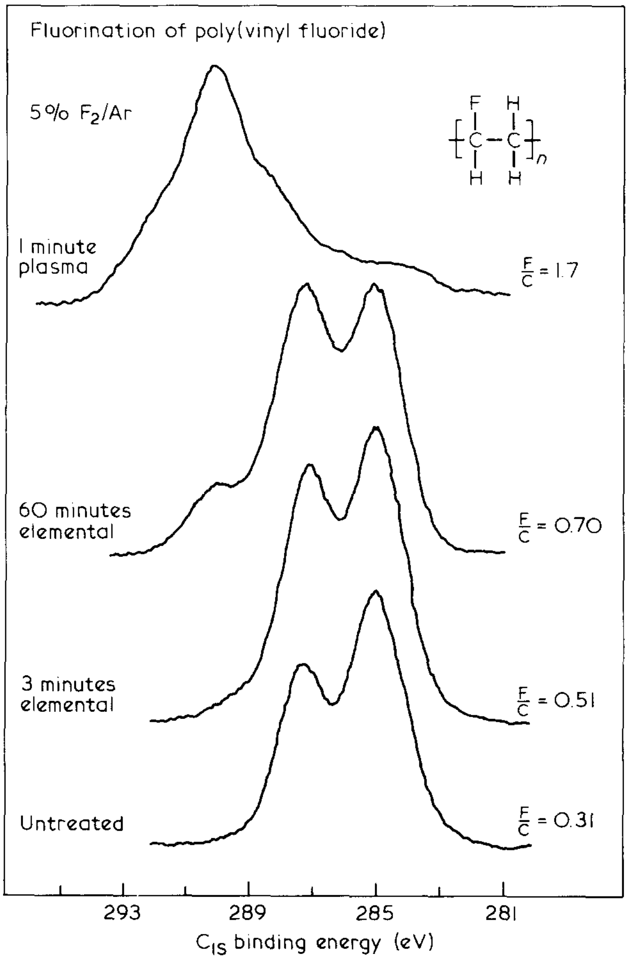

Figure 2 C_{1s} e.s.c.a. spectra of untreated and reacted poly(vinyl fluoride) film

There has been some controversy concerning the rate limiting process in the elemental reaction. The model polymers used in this study clearly demonstrate that intrinsic kinetic limitations are encountered when perfluorinating polymer surfaces with elemental fluorine.

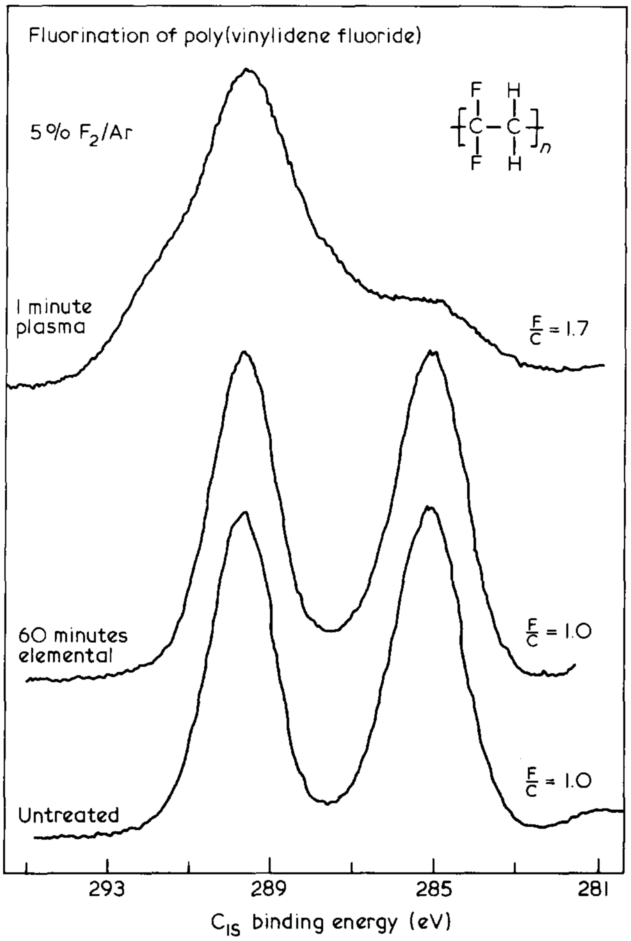

Figure 3 C_{1s} e.s.c.a. spectra of untreated and reacted poly(vinylidene fluoride) film

The reported data are not consistent with a diffusion limited surface reaction. The variance in diffusion coefficients due to chemical and/or morphological differences among the polymers cannot account for the range of observed reaction rates[10]. Also, the plasma cannot increase the mass transfer of fluorine enough to account for the faster reaction rate in this environment. Finally, the presence of intermediate reaction products, such as –CHF– in the PE reaction, is contrary to the definition of a mass transfer rate limited reaction. The relative success of the plasma environment is a consequence of enhanced intrinsic reaction kinetics.

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