Synthetic Applications of Molecular Beams

David C. Weber,* Andrew P. Baronavski, Thomas P. Heavner, and Clarence L. Gordon, III

Chemistry Division, Naval Research Laboratory, Washington D.C. 20375, U.S.A.

Polymer films have been successfully modified using reactive species generated in a pulsed supersonic beam.

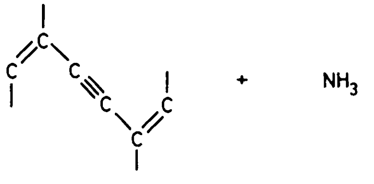
The pulsed supersonic beam technique has been used successfully for the production of molecular beams of both stable and transient species for spectroscopic studies.[1,2] Photolysis of the molecules in the beam can produce a wide variety of molecular fragments (other molecules, radicals, charged species). We have applied this technique to the modification of polymer surfaces to promote novel chemical reactions not readily accessible by standard techniques. This technique could also be viewed as an extension of our ion-implantation work,[3,4] but where the translational energies are of the order of 1 eV, an energy regime in which dissociation is negligible and penetration is not a factor.

We have attempted to modify polyethylene, polystyrene, polyacetylene, and polyvinylidene difluoride (PVF_2) using this technique. The beams used in the modification of the polymers were made from HN_3. Photolysis of the HN_3 beam was accomplished using a pulsed excimer laser at 193 or 248 nm. The laser was synchronized to the molecular beam pulses to produce 99% NH and N_2 in the region just above the surface of the polymer. In a typical experiment molecular beam pulses of 200 μs duration with a repetition rate of 10 Hz were used. The pressure in the beam chamber was maintained at $<10^{-4}$ Torr during the pulse. Typically, the gas reservoir for the pulsed beam was at 2 atm and consisted of 10% HN_3 in He. Experiments were conducted for 20 minutes to 1 h. Under these conditions approximately 10^{17}—10^{19} reactant species hit the surface of a sample during each experiment. The resultant films were then analysed by *X*-ray photoelectron spectroscopy (X.p.s.), i.r. and Fourier transform i.r. (F.t.i.r.) spectroscopy, as well as 4 point probe DC conductivity measurements.

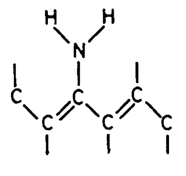
The polymer film having the greatest reactivity towards the NH radical was the polyacetylene film. Experiments were conducted with the laser beam off to evaluate the effect of the unphotolysed beam on the polymer. In each case, changes in measured properties of the films were not observed. Therefore, any changes to the films in the experiments with the laser on could be attributed to the presence of the radicals in the beam. An interesting observation was made during the NH + $(CH)_x$ experiment. A chemiluminescence occurred in the region directly above the $(CH)_x$ film. This glow was absent when the $(CH)_x$ was removed from the beam or if a different polymer film was used. Although attempts were not made to characterize the nature of the emission at this point, we believe that the emission was due to an interaction of the backscattered beam with the incoming beam. This belief is based on the colour of the emission which we observed and characterized in previous studies. The pristine polyacetylene films used in this experiment had a silvery metallic appearance. After bombardment with the NH beams the films turned a golden colour. The colour change is reproducible and the intensity of the colour is a function of the flux of the radicals.

We believe that exposing $(CH)_x$ to a pulsed beam of NH ($^1\Delta$) radicals leads to one of the radical–substrate interactions shown in (I), (II), and (III). A variety of spectroscopic techniques was employed to determine which of the proposed structures occurs.

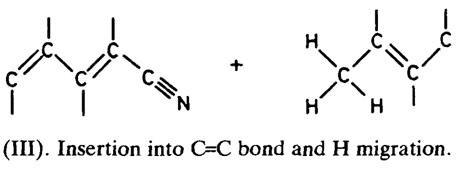
A peak at approximately 2100 cm^{-1} attributable to C≡N is seen in the transmission and F.t.i.r. spectra after exposure to the NH ($^1\Delta$) beam (Figure 1). Analysis of the *cis*- (750 cm^{-1}) and *trans*- (1010 cm^{-1}) absorption ratios did not show any change as a result of exposure to the beam. X.p.s. analysis indicated that the surface region contained approximately 70% nitrogen (Figure 2). The observed nitrogen was present in a reduced state (*i.e.* $-NH_2$, C≡N). The somewhat broadened N 1s line indicates the possibility of more than one type of nitrogen interaction. No evidence of attenuation of lower kinetic energy photoelectrons was found. This is consistent with the modification being restricted to the near surface



(I). H Extraction.



(II). Insertion into C–H bond.



(III). Insertion into C=C bond and H migration.

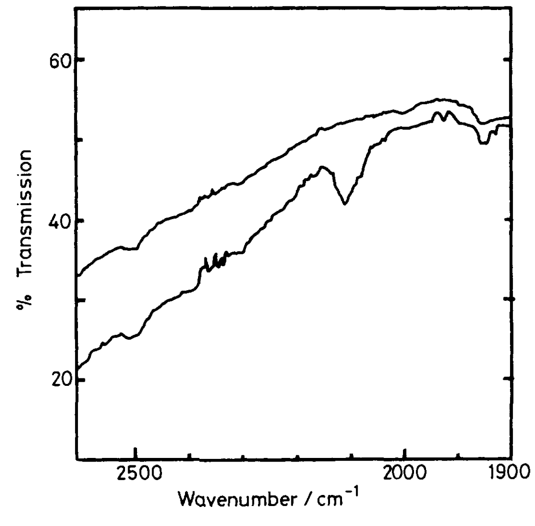


Figure 1. I.r. spectrum from 2600 cm^{-1} to 1900 cm^{-1} of the polyacetylene before and after exposure to beam.

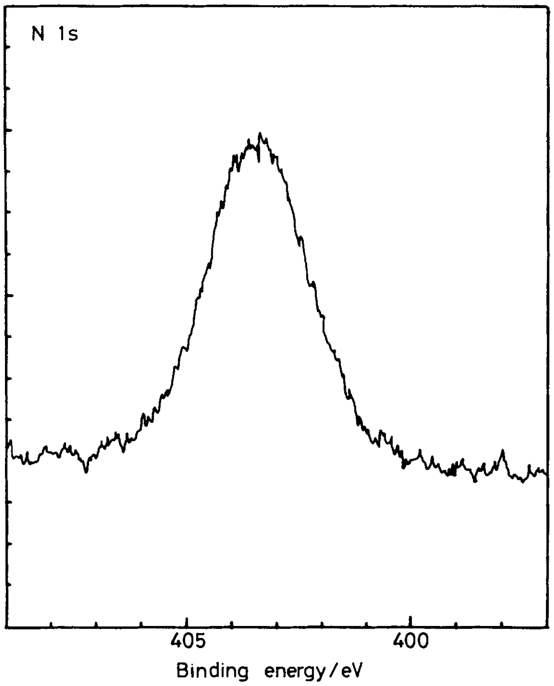


Figure 2. X.p.s. spectrum of the polyacetylene after exposure to beam.

region. Four point probe conductivity measurements were made before and after exposure to the beam. After exposure, a reproducible 50% decrease in the conductivity was measured. Our data are most consistent with interaction (III) as the predominant reaction pathway. Work is proceeding to characterize further the products of this interaction. Similar experiments with PVF2, polystyrene, and polyethylene did not show any evidence of direct reaction with the NH beam. This is probably due to the double bond reactivity in the $(CH)_x$ backbone compared with the saturated backbones of the other polymers initially studied. Other polymer films are presently being produced for reactivity screening.

Our results demonstrate the utility of molecular beams for synthetic applications. The technique appears to have promise in modifying the surface of reactive polymers. In this case a polymer, polyacetylene, that is quite intractable and not easily modified once formed into a film, was readily modified. By selecting the molecular beam and the appropriate photolysis frequency, the type of modification can be controlled.

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