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Reactions of Atomic Oxygen [$O(^3P)$] with Polybutadienes and Related Polymers

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Thin films of the following polymers were exposed at ambient temperature to ground-state oxygen atoms [$O(^3P)$], generated by a radio-frequency glow discharge in O_2 : *cis*- and *trans*-1,4-polybutadienes (CB and TB), amorphous 1,2-polybutadiene (VB), polybutadienes with different 1,4/1,2 contents, *trans* polyentenamer (TP), *cis* and *trans* polyoctenamers (CO and TO), and ethylene-propylene rubber (EPM). Transmission infrared spectra of CB and TB films revealed extensive surface recession, or etching, unaccompanied by any microstructural changes within the films, demonstrating that the reactions were confined to the surface layers. Contrary to the report by Rabek, Lucki, and Rånby (1979), there was no $O(^3P)$ -induced *cis-trans* isomerization in CB (or TB). From weight-loss measurements, etch rates for polybutadienes were found to be markedly dependent on vinyl content, decreasing by two orders of magnitude from CB (2% 1,2) to structures with 30-40% 1,2 double bonds, thereafter increasing by half an order of magnitude to VB (97% 1,2). Relative etch rates for EPM and the polyalkenamers were in the order: EPM > CO (or TO) > TP > CB. The sole non-elastomer examined, TB, had an etch rate about six times that of CB, ascribable to a morphology difference. *Cis/trans* content had a negligible effect on the etch rate of the polyalkenamers. Mechanisms involving crosslinking through vinyl units are proposed for the unexpected protection imparted to polybutadienes by the 1,2 double bonds.