'Living' Free-radical Copolymers prepared from Perfluoro-2,5-diazahexane-2,5-dioxyl

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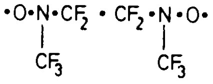
Summary Stable, 'living', free-radical copolymers with number-average molecular weights in the range 1250—11,000, prepared by reaction of an excess of perfluoro-2,5-diazahexane-2,5-dioxyl with fluoro-olefins, react, *via* the terminal nitroxide groups, with fluoro-olefins, sulphur dioxide, or perfluorobuta-1,3-diene to give copolymers of enhanced molecular weights; unsaturated nitroso rubbers prepared by reaction of perfluorobuta-1,3-diene with 'living' copolymers prepared from hexafluoropropene and the dioxyl have been successfully cross-linked with 'living' copolymers.

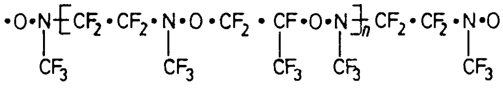
The preparation of perfluoro-2,5-diazahexane-2,5-dioxyl, (**1**), opened a new route to the synthesis of nitroso rubbers, and transparent, colourless, 1 : 1 alternating copolymers have been obtained by the reaction of (**1**) with an excess of fluoro-olefin.[1] The reaction of a fluoro-olefin with an excess of the dioxyl has now given 'living' copolymers, *e.g.* (**2**) from hexafluoropropene at room temperature. The excess of (**1**) and the 1 : 1 cyclic adduct (**3**) were removed by pumping to leave a viscous oil. These, the first linear, bifunctional, 'living,' stable, free-radical copolymers to be prepared, are inert towards water, air, and glass at room temperature, as is (**1**) and its monofunctional analogue bistrifluoromethyl nitroxide. Samples stored for several months in stoppered ampoules remained active.

The molecular weights of the 'living' copolymers were determined by end-group analyses. These involved titration of the iodine liberated from an excess of aqueous potassium iodide at room temperature by a weighed quantity of 'living' copolymer dissolved in $CF_2Cl.CFCl_2$ [1 mole (**1**) or 1 mole 'living' copolymer → 1 mole I_2]. Molecular weights were also determined by spectrophotometry since solutions of (**1**) and of 'living' copolymers in $CF_2Cl.CFCl_2$ absorb at 535 nm. Molecular weight determinations on a copolymer (**2**) were 2240 (KI) and 2350 (spectrophotometry). Varying the ratio (**1**) : C_3F_6 gave 'living' copolymers with molecular weights in the range *ca.* 1250—11,000.

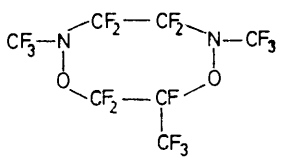
'Living' copolymers react readily with fluoro-olefins and with perfluorobuta-1,3-diene at room temperature. Thus, the reaction of an outgassed solution of the copolymer (**2**) ($\overline{M}_n$ *ca.* 2300) in $CF_2Cl.CFCl_2$ with an excess of C_4F_6 was complete by the time the reaction mixture had warmed from -196 °C to room temperature. The new colourless copolymer [$(\eta) = 0{\cdot}09$ dl g^{-1} in $(C_4F_9)_3N$ at 30 °C, $\overline{M}_w$ *ca.* 36,000†] obtained as the involatile residue contained residual unsaturation (i.r., ^{19}F n.m.r. spectroscopy) corresponding to both 1,2- and 1,4-additions of 'living' copolymer molecules to the diene. It was successfully cured after being mixed with a 'living' copolymer (**2**) (11·8% w/w) of mole-

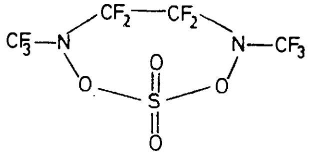

$\cdot O\cdot \underset{CF_3}{N}\cdot CF_2\cdot CF_2\cdot \underset{CF_3}{N}\cdot O\cdot$

(1)


$\cdot O\cdot \underset{CF_3}{N}\left[CF_2\cdot CF_2\cdot \underset{CF_3}{N}\cdot O\cdot CF_2\cdot \underset{CF_3}{CF}\cdot O\cdot \underset{CF_3}{N}\right]_n CF_2\cdot CF_2\cdot \underset{CF_3}{N}\cdot O\cdot$

(2)


(3)


(4)

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† Calculated using the equation $[\eta] = 8{\cdot}77 \times 10^{-5} \overline{M}_w^{0{\cdot}66}$ which relates $\overline{M}_w$ and $[\eta]$ of CF_3NO–C_2F_4 copolymers in $(C_4F_9)_3N$ at 25 °C (G. A. Morheau, P. I. Roth, and A. R. Schultz, *J. Polymer Sci.*, 1961, **55**, 609).

cular weight *ca.* 1900 (spectrophotometry) and heated in a press (1000 p.s.i.) at 140 °C for 1 h [vulcanizate gel content 93·1%, V_r (*i.e.* ratio of volume of dry rubber to volume of swollen network) = 0·49, equilibrated in $CF_2Cl.CFCl_2$ at 30 °C for 3 days].

A solution of the 'living' copolymer (**2**) in $CF_2Cl.CFCl_2$ reacted with SO_2 in a sealed evacuated tube (10 days in darkness at room temperature) to give a copolymer containing $\mathrm{O{=}\overset{|}{\underset{|}{S}}{=}O}$ units (i.r. spectrum). Reaction of (**1**) with SO_2 under similar conditions was complete within 1 h giving not a copolymer, but the cyclic adduct (**4**) [96% based on (**1**)], the structure of which was established by elemental analysis and spectroscopy (i.r., ^{19}F n.m.r., and mass). Bistrifluoromethyl nitroxide reacts at room temperature with SO_2 (3 days) to give the compound $(CF_3)_2N.O.SO_2.O.N(CF_3)_2$ [97% based on $(CF_3)_2NO\cdot$] (*cf.* 44% yield from the reaction at 180 °C).[2] The preparation of block copolymers using 'living' copolymers is currently under investigation.

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