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Journal of Fluorine Chemistry 127 (2006) 426–432
JOURNAL OF FLUORINE CHEMISTRY
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EPR studies on regio-selective H-abstraction by ''magic blue'' reagent from polymers

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Received 18 November 2005; received in revised form 12 January 2006; accepted 13 January 2006
Available online 23 February 2006

Abstract

The radical reactions of polyolefin and olefin copolymers (**4–9**), polydienes and diene coplymers (**10–15**), and polysiloxane (**16**) with ''magic blue'' reagent containing H-abstracting agent-bis{perfluoro-1-[1-(2-fluorosulfonyl)ethoxy]ethyl}nitroxide $[FSO_2CF_2CF_2OCF(CF_3)]_2N(O^\bullet)$ (**2**)and spin trap-perfluoro-1-nitroso-[1-(2-fluoro-sulfonyl)ethoxy]ethane $FSO_2CF_2CF_2OCF(CF_3)NO$ (**3**) were studied by EPR detection of the spin adducts of the corresponding polymeric radicals generated in the H-abstraction step to the spin trap **3**, namely, the nitroxides $FSO_2CF_2CF_2OCF(CF_3)N(O^\bullet)$ (polymer-H) **17–29**. EPR studies have provided information about the regio-selectivity of H-abstraction, the subsequent radical steps followed H-abstraction and grounded a possibility of employing ''magic blue'' reagent in polymer modification via H-abstraction-initiated grafting polymerization.

Keywords: Polyolefin; Olefin copolymer; Polydiene; Diene copolymer; Polysiloxane; Magic blue reagent; Hydrogen abstraction; Spin trapping

1. Introduction

In the present days, free radical grafting polymerization is usually initiated by H-abstraction with alkoxy radical generated in decomposition of peroxide at rather high temperature [1]. These radical processes are often accompanied with poor regio-selectivity and unavoidable degradation of the polymer substrates [2].

''Magic blue''—the blue F113 ($CClF_2$–CCl_2F) solutions containing very effective H-abstracting agent bis[perfluoroalkyl]nitroxide $R_fN(O^\bullet)R_f$ and nitroso spin trap R_fNO both generated in the reaction of per(poly)fluoroalkyl peroxide $(R_fCO_2)_2$ with $NaNO_2$ were firstly reported by Zhao and co-workers [3] and used in the study of H-abstraction reactions at room temperature from many kinds of substrates such as alkanes and arylakanes [4], aldehydes [5], ethers [6], alcohols [7], pyrimidines [8] and silicons [9]. The radical(s) generated in the H-abstraction step and/or in the subsequent radical step(s) was (were) immediately trapped by R_fNO. From the well resolved EPR spectra of various spin adducts, a large number of fluorinated nitroxides (FN) of a wide variety of structures have been identified and much valuable information about structures and mechanisms was gained.

Following the above mentioned studies on H-abstraction from organic substrates, the first success in polymer modification by putting using of ''magic blue'' reagent is regio-selective H-abstraction initiated grafting polymerization of perfluorovinyl monomer onto polystyrene [10]. In order to find out application of our technique among other polymers, in this paper, we reported an EPR study of highly selective H-abstraction from polyolefin and olefin copolymers (**4–9**), polydienes and diene coplymers (**10–15**), and polysiloxane (**16**) by ''magic blue'' reagent containing bis{perfluoro-1-[1-(2-fluorosulfonyl)ethoxy]ethyl}nitroxide$[FO_2SCF_2C$-$F_2OCF(CF_3)]_2$-$N(O^\bullet)$ (**2**) and spin trap perfluoro-1-nitroso-[1-(2-fluorosulfonyl)ethoxy]ethane $FSO_2CF_2CF_2OCF(CF_3)NO$ (**3**) dissolved in F113 solution at room temperature.

2. Results and discussion

2.1. Polymer substrates in H-abstraction/trapping process

The polymer substrates subjected EPR study in H-abstraction/traping process with ''magic blue'' reagent (**2 + 3**) are polyolefin and olefin copolymers (**4–9**), polydienes and diene coplymers (**10–15**), and polysiloxane (**16**) as shown

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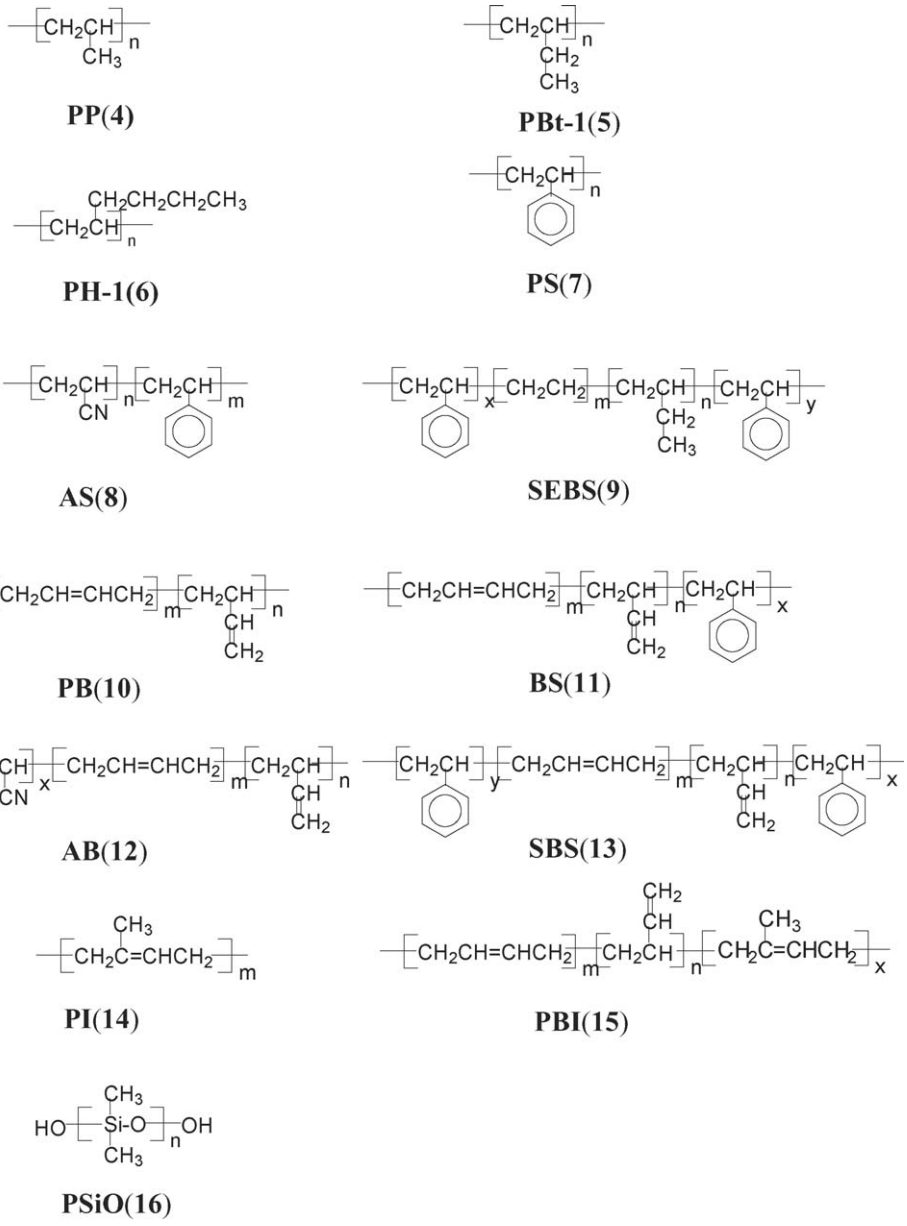
0022-1139/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.jfluchem.2006.01.006

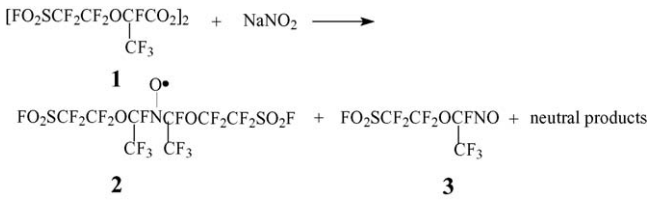


Scheme 1. The polymer substrates.

in Scheme 1. The polyolefin and olefin copolymers (**4–9**) bearing tertiary-hydrogen atoms usually reacted as H-donors with oxygenated radicals in their reactive processing in molten state. The polydiene and diene copolymers (**10–15**) contain C=C double bonds and allyl units. The allylic hydrogens are expected to be selectively abstracted by nitroxide **2** from view points of both kinetic (bond dissociation energy) and thermodynamic stability of polymer radical intermediate. The methyl hydrogen in polysiloxane can also be abstracted since the α-silicon with d-orbital may stabilize the resulted methyl radical intermediate [9].

2.2. Preparation and EPR identification of ''magic blue'' (2 + 3)

In a typical procedures, perfluoro-di[1-(2-fluorosulfonyl)ethoxy]propyonyl peroxide **1** in F113 was added into a deoxygenated glass bottle with an excess of dry powered sodium nitrite. After shaking several minutes, a blue color (indicator of nitroso-trap **3**) appeared and developed. The reaction mixture was cooled in icy-water bath for 1–2 h until the disappearance of the peroxide. Then strong and well resolved EPR spectrum of nitroxide **2** could be recorded. The radical process generating ''magic blue'' is shown in Scheme 2. The EPR spectra of bis{perfluoro-1-[1-(2-fluorosulfony-



Scheme 2. Generation of magic blue (**2 + 3**).