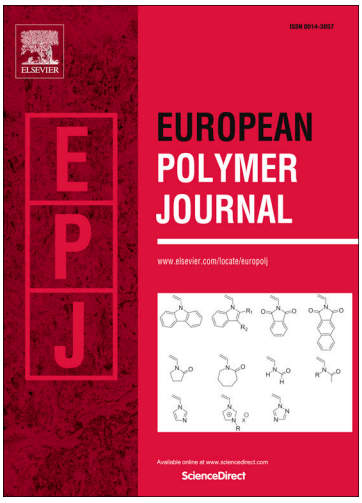

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A new approach to improvement of gas permeation properties of metathesis polynorbornenes: *gem*-difluorocyclopropanation of backbone double bonds

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ABSTRACT

The impact of double bond modification by gem-difluorocyclopropanation (gDFC) in poly(norbornenes) backbone on their gas transport properties was studied for the first time. With this aim the research of gDFC of polynorbornene (PNB) and poly(5-trimethylsilylnorbornene) (PNBSi) in the conditions of sodium chlorodifluoroacetate thermolyses at 180-190^{o}C in methyl benzoate solution were carried out. The starting poly(norbornenes) were synthesized via ring-opening metathesis polymerization of the corresponding monomers mediated by the first generation Grubbs' catalyst. The degree of double bonds conversion into the gem-difluorocyclopropane and the molecular weight of modified polymers could be controlled by adjusting the reaction time, sodium chlorodifluoroacetate amount, and polymer concentration in reaction mixture, as well as by addition of inhibitor. The bulky Me_3Si-substituent hindered the modification of double bonds in poly(norbornenes)' backbone. The gDFC decreased the thermal stability of poly(norbornenes). However, the films of modified polymers demonstrated high stability during storage at the ambient conditions, especially in comparison with unmodified polynorbornene. The introduction of gem-difluorocyclopropane in poly(norbornenes) backbone increased their gas permeability coefficients P especially strongly for PNB. Simultaneously the values of ideal selectivity $\alpha_{ij}=P_i/P_j$ were not changed or slightly increased. The noted growth of P was caused by increases in the solubility coefficients S. To elucidate the role of the two types of

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