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LETTERS TO THE EDITOR

Polymerization of Norbornene in the Presence of Catalysts on the Basis of Palladium Acetate and Boron Trifluoride Etherate

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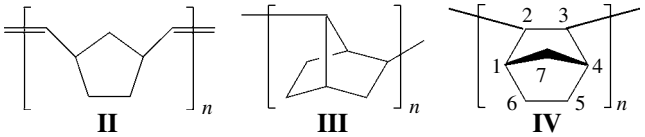
Norbornene (bicyclo[2.2.1]hept-2-ene) (**I**) and its derivatives can undergo methathesis, radical, cationic, or additive polymerization to form polymers **II**, **III**, or **IV**, respectively. The additive polymerization involves rupture of the double bond to form polymers with specific properties necessary for the production of coating in electronics, telecommunication materials, optic lenses, substrates for plastic displays, photoresistors for chips and displays, and dielectrics for semiconductors [1, 2].



II **III** **IV**

In the present communication we describes a highly effective catalytic system on the basis of palladium carboxylates $Pd(RCOO)_2$ and $BF_3 \cdot OEt_2$, for additive polymerization of norbornene.

The conditions of a standard experiment are as follows: Pd 1.0×10^{-6} mol, B : Pd molar ratio 25, **I** : Pd molar ratio 5×10^4 (4.71 g of norbornene), reaction time 30 min, temperature 25°C, solvent toluene, total volume of the reaction mixture 7 ml. The polymerization of norbornene was performed in a glass reactor with a magnetic stirrer under an inert gas (nitrogen, argon).

As the temperature of the $Pd(OAc)_2$–$25BF_3 \cdot OEt_2$ system is increased from 25 to 65°C, the conversion, as well as the characteristic viscosity of the resulting polymers much decrease. As the **I** : Pd ratio is varied from 25 000 to 100 000 at a constant catalyst concentration, the conversion of norbornene into polymers is almost invariable, but the characteristic viscosity of the polymers decreases.

When the quantity of the palladium catalyst is 1.0×10^{-5} mol, the catalytic activity reaches more than 150 000 kg norbornene per 1 mol Pd per hour. Such activity compares with the best reported results [3–6] and is about 7 times that of the $Pd(acac)_2$–$25BF_3 \cdot OEt_2$ system [7].

The NMR and IR spectral data show that the structure of the resulting polymers corresponds to the additive type. The ^1H NMR spectrum lack double-bond proton signals. The IR spectrum, too, lacks bands at 1620–1680 cm^{-1} ($\nu_{C=C}$) but shows strong bands characteristic of bending vibrations of bridging CH_2 groups of the norbornene ring at 1452–1474 cm^{-1} [8]. The ^{13}C NMR signals at 28–34 ppm relate to C^5 and C^6, according to their numbering in formula **IV**. The bridging atoms C^7 give signals at 34–38 ppm. The bridgehead atoms C^1 and C^4 appear at 38–45 ppm. The signals at 45–55 ppm relate to the C^2 and C^3 atoms of the main chain of the polymer. The lack of signals at 20–24 ppm points to *exo* configuration of the polymeric chain [9]. The C^7 signal in the ^{13}C NMR spectrum appears as a single group of strong signals at 34–38 ppm, which suggests that the polymer microstructure is a composition of *rr* and *mr* triads with low diisotacticity [10]. Evidence for the lack of mm triads is provided by the absence of a resonance signal at 39 ppm [9].

The molecular weight of the polymers measured by means of gel-permissive chromatography (reference polystyrene) is within the range M_w 77 700–293 800 D. The molecular weight distribution Q =

M_w/M_n for polymerization in the standard conditions is close to 2, which is a theoretical value for the Flory–Schulz distribution for ideal polymerization with chain termination. This value suggests single-center homogeneous active complexes. The thermal degradation point of the polymers varies from 313 to 324°C (TGA), whereas their glass point, from 240 to 262°C (DSC).

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