# **Cationic Reactivity of Olefins Present in the C<sub>5</sub> Fraction**

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A study of the cationic reactivity of olefins present in the  $C_5$  fraction has been performed under conditions similar to those used for synthesis of hydrocarbon resins. The most important olefins present in the  $C_5$  fraction, viz. 2-methyl-1-butene, 2-methyl-2-butene, 1-pentene, cyclopentene, *cis*-2-pentene, *trans*-2-pentene, and 3-methyl-1-butene, were considered. Their relative reactivities were evaluated by using cyclopentene as a standard reference monomer in a series of copolymerizations at 40 °C in cyclohexane solution in the presence of AlCl<sub>3</sub>-HCl--xylene complex as catalyst. Owing to the very low molecular weight values of the resulting oligomers, the systems were considered as copolymerizations in which transfer to monomer is operative. A copolymerization equation including monomer transfer was proposed from which the *R* parameters, related to the propagation and chain-transfer reaction, were obtained. The equation, by using the Kelen-Tüdös treatment, fits very well the experimental results, and the *R* values were obtained for the various pair of monomers. The system show almost ideal behavior, and a reactivity order for the olefins was obtained.

## Introduction

The use of the  $C_5$  hydrocarbon fraction for producing hydrocarbon resins is an important industrial application of cationic catalysts.<sup>1</sup> The  $C_5$  fraction produced in the steam cracking of naphthas contains about 50% of olefins and dienes which can react, to different extents, in the polymerization process and allow the production of hydrocarbon resins having different properties. Despite the existence of many patents on the cationic polymerization of the  $C_5$  fraction, no data are available on the relative reactivities of the monomers in the reacting system.

As a part of research on the utilization of the  $C_5$  fraction in cationic reactions, a systematic study on the relative reactivities of the  $C_5$  monomers has been undertaken. We first considered the most important olefins present in the  $C_5$  fraction, and then the dienes and the other unsaturated hydrocarbons were taken into account.

In this work, a comparison of the cationic reactivities of the  $C_5$  olefins with cyclopentene, as a reference comonomer, is reported using experimental conditions similar to those adopted for synthesis of hydrocarbon resins.

#### **Experimental Section**

**Reagents.** The monomers, 3-methyl-1-butene, 2-methyl-1-butene, 2-methyl-2-butene, *cis*-2-pentene, *trans*-2pentene, 1-pentene, and cyclopentene, were Fluka products, pure grade (GC purity >99%). Cyclohexane, *n*-hexane, aluminum chloride, hydrochloric acid, and xylene were RPE Carlo Erba products, purified as previously reported.<sup>2</sup>

The catalyst was obtained by bubbling anhydrous hydrochloric acid at atmospheric pressure into a stoichiometric slurry of  $AlCl_3$ -xylene until a homogeneous solution was obtained. The analysis performed on the obtained catalyst showed that the molar ratio between the components HCl,  $AlCl_3$ , and xylene was 0.5:1.09: 1.15.

**Copolymerization.** The copolymerizations were carried out in glass microreactors, volume about 15 mL, equipped with a magnetic stirrer and a sealed port for introduction of the reagents or withdrawal of the products by means of a syringe. The monomer mixture was maintained at the selected temperature (40 °C) using a thermostatic bath. For each run, 4 mmol of reagents was used per 10 mL of reaction volume.

Copolymerization was started by introducing the catalyst (about 0.05  $\mu$ mol of AlCl<sub>3</sub>), and after 5 min water containing 5% NH<sub>4</sub>OH was added. Each pair of monomers was tested by a series of runs with initial monomer molar ratio in the range between 3:1 and 1:3. To consider the microreactor as a differential one, only results of experiments in which the conversion for both monomers was lower than 10% has been taken into account. All manipulations of monomers and catalyst were carried out under dry N<sub>2</sub>.

Analyses. The compositions of the copolymers were determined by GC analysis of the residual monomers in the sample withdrawn from the reaction mixture; a programmed temperature increase (3 min at 25 °C, 10 °C/min up to 75 °C) on a Varian 3700 instrument equipped with a DB-1 J&W megabore column, a FID detector, and a Varian 4270 integrator was used.

The  $M_n$  values of the samples were determined by means of a Knauer vapor pressure osmometer equipped with Digital Meter G06. GPC measurements were carried out with a Waters Instruments HPLC by using THF as solvent, Styragel columns, PL50, 100, 500 and 10 000 A, and a refractive index detector.

### **Results and Discussion**

The reactivities of the olefins were tested in a series of copolymerizations carried to low conversion using cyclopentene as a reference monomer. Cyclopentene was selected because of its abundance and reliable GC determination.

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