Polymer Bulletin 6, 55-60 (1981)

Polymer Bulletin

Initiation of Cationic Polymerizations with Alcohol/Lewis Acid Systems

2. Model Study with 2,4,4-Trimethyl-1-Pentene

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Preparatory to polymerization studies with the $R^tOH/BCl_3/$ isobutylene system, model reactions have been carried out using 2,4,4-trimethyl-1-pentene as a model for isobutylene and 1,1-diphenyl ethanol and 2-phenyl-2-propanol as tertiary alcohols in CH_2Cl_2 at -50°C. According to results of ^1H and ^{13}C NMR and IR spectroscopy, the reactions start by ionization of the tertiary alcohol ($R^tOH + BCl_3 \rightleftharpoons R^{t\oplus}BCl_3OH^{\ominus}$) and proceed by olefin cationation ($R^{t\oplus} + C{=}C \longrightarrow R^t\text{-}C\text{-}C^{\oplus}$). Indane skelton formation is an important reaction in these model experiments.

Introduction

We have discovered that tertiary alcohols in conjunction with BCl_3 initiate the polymerization of isobutylene in polar solvent[1]. Subsequently, we have investigated the fundamentals of this new initiating system and carried out model experiments with tert-alcohol/BCl_3 combinations in the absence of olefins[1]. It was concluded that these reactions start by the BCl_3 ionizing the alcohol and yield the ion pair $R^{t\oplus}BCl_3OH^{\ominus}$, which in the presence of a suitable olefin induce the polymerization. Preparatory to detailed polymerization experiments, we wanted to elucidate further the mechanism of initiation and decided to mimic isobutylene polymerizations by the nonpolymerizable branched olefin 2,4,4-trimethyl-1-pentene (TMP), an excellent model for isobutylene[2,3,4]. We postulated that cationation in the R^tOH/BCl_3/TMP system will proceed by the $R^t\text{-}TMP^{\oplus}BCl_3OH^{\ominus}$ ion pair whose even fleeting existence could be demonstrated by analyzing the products of suitable model experiments. This paper describes experiments in this direction, in particular, investigations with the tertiary alcohols 1,1-diphenyl ethanol ($C\varnothing_2COH$) and 2-phenyl-2-propanol ($C_2\varnothing COH$) plus BCl_3, and TMP using CH_2Cl_2 solvent at -50°C under high vacuum conditions. Spectroscopic (^{13}C and ^1H NMR, IR) analyses indicate that our basic assumptions were correct; however, side reactions have to be taken into consideration, e.g., indane skeleton formation by intramolecular alkylation.

Experimental

Experiments were carried out under high vacuum in an all glass (Pyrex) reactor with magnetic agitation. Chemicals were carefully purified and dried[5]. Typically, we added BCl_3 (1 ml) to mixtures of CH_2Cl_2 (≅50 ml), alcohol (≅1 g) and TMP (3 ml) at -50°C. After 30 minutes a prechilled methanol/CH_2Cl_2 solu-

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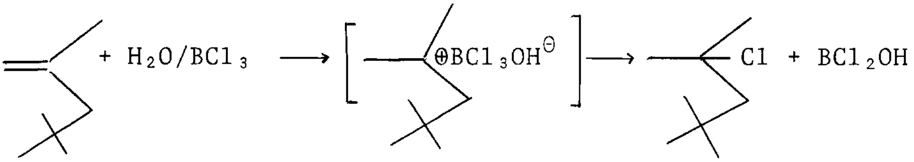
tion was added, the system was washed with acidified water and dried over $MgSO_4$. Volatile components were removed by distillation. ^{13}C and ^1H NMR (300 MHz) and IR analyses were carried out by the use of $CDCl_3$ or CCl_4 solutions with Varian (300 MHz, CFT-20) and Perkins-Elmer 521 spectrometers.

Results and Discussion

Kennedy et al.[2,6] have studied the H_2O/BCl_3/TMP model system and postulated the following reaction:



A similar reaction path is likely to be operational in R^tOH/BCl_3/TMP systems.

Figure I shows the ^1H NMR spectrum obtained for the $C_2\emptyset COH/BCl_3$/TMP system together with the assignments. The resonance at 6.9 ppm indicates the presence of an indane skeleton[6]. The presence of a substituted indane has been confirmed by ^{13}C NMR (Figure II, resonances at 150 and 152.9 ppm corresponding to two quaternary carbons common to two rings) and IR spectroscopy (Figure IIIa; the absence of a vibration at 700 cm^{-1} indicates the absence of tertiary chloride). Evidently the $C_2\emptyset COH/BCl_3$/TMP experiment yielded mainly 1-neopentyl-1,3,3-trimethylindane[1]. The most likely reaction path is as follows:

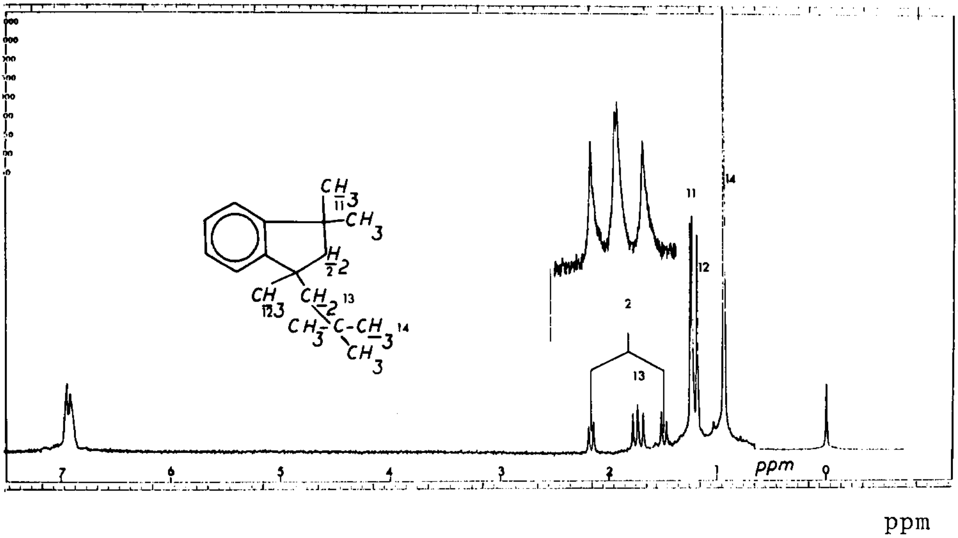


Figure I: ^1H NMR spectrum of 1-neopentyl-1,3,3-trimethylindane

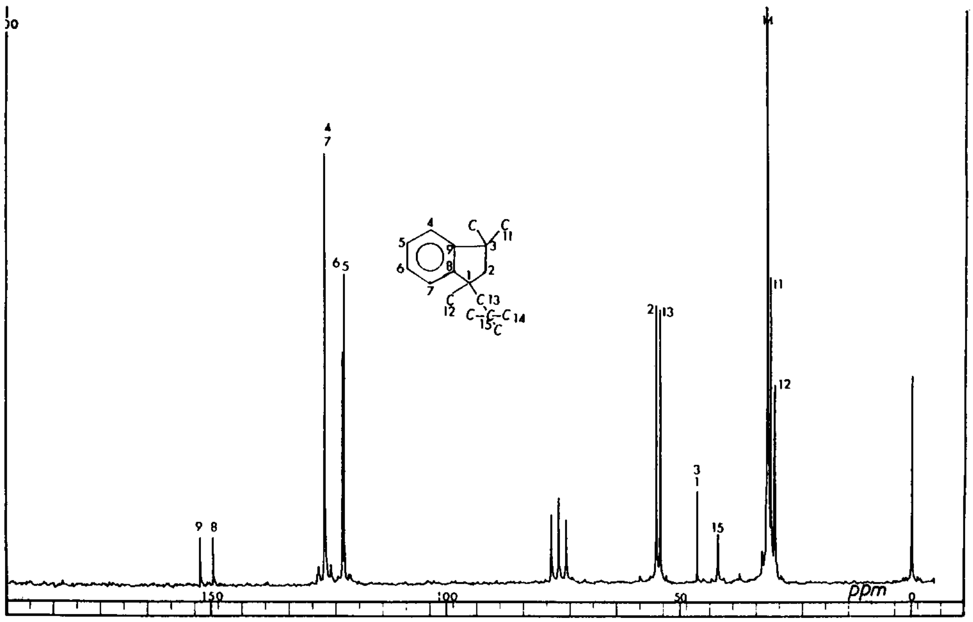


Figure II: ^{13}CMR spectrum of 1-neopentyl-1,3,3-trimethylindane

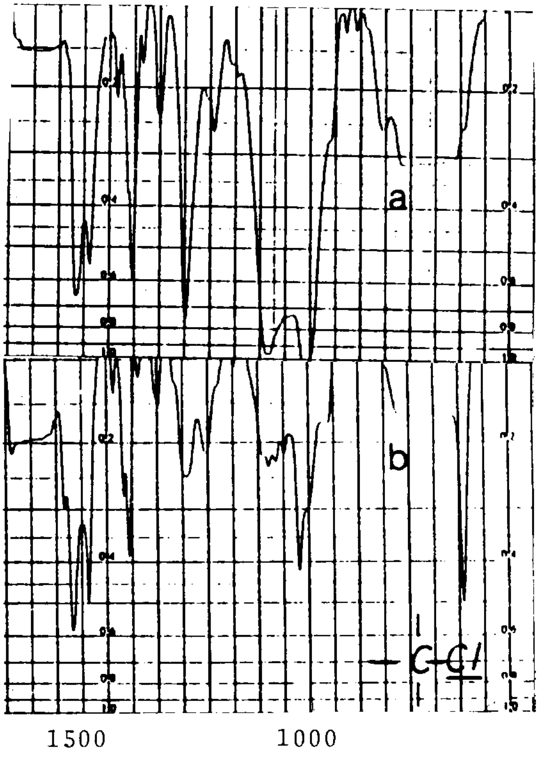
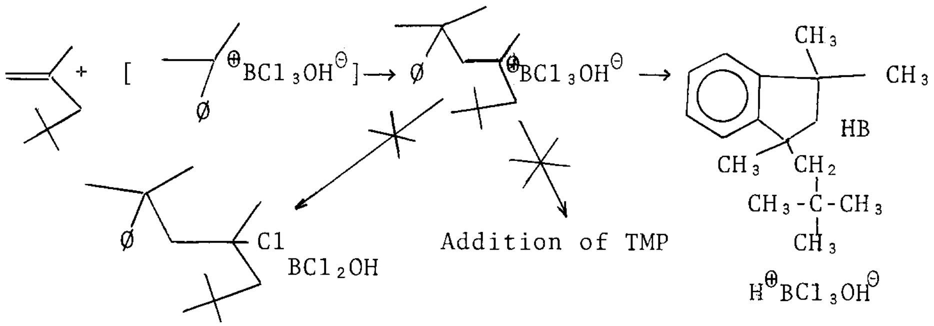
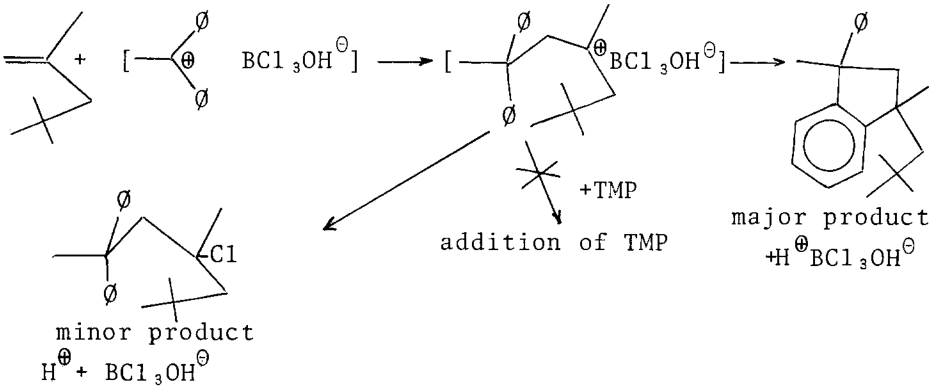


Figure III: IR spectra of (a) 1-neopentyl-1,3,3-trimethylindane and (b) 1-neopentyl-1,3-dimethyl-3-phenylindane + 4-chloro-2,2,4,6,8,8-hexamethyl-6(2',2'-diphenyl)-propylnonane



Subsequently, we investigated the $C\text{Ø}_2COH/BCl_3$/TMP model system and Figures IV and V show respectively the ^1H and ^{13}C NMR spectra together with assignments. The main product is again the indane derivative (∿95%); however, a small amount (∿5%) of linear product is also evident (proton resonances at a=1.02, b=2.45, c=0.97, d=1.64, e=3.05 and f=1.84 ppm). The presence of linear product is also indicated by a vibration at 700 cm^{-1} in the IR spectrum of the product mixture (Figure IIIb). On the basis of these evidences, the most likely reaction path in this system is as follows:



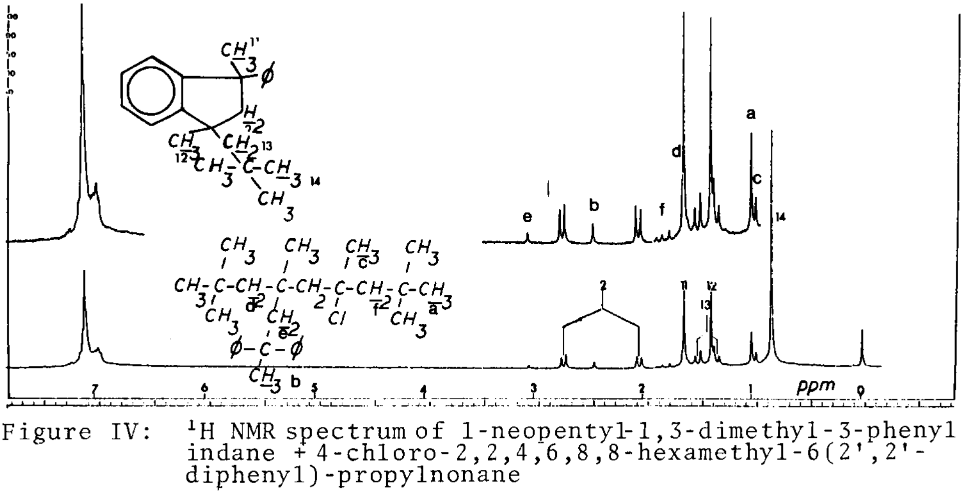


Figure IV: ^{1}H NMR spectrum of 1-neopentyl-1,3-dimethyl-3-phenylindane + 4-chloro-2,2,4,6,8,8-hexamethyl-6(2',2'-diphenyl)-propylnonane

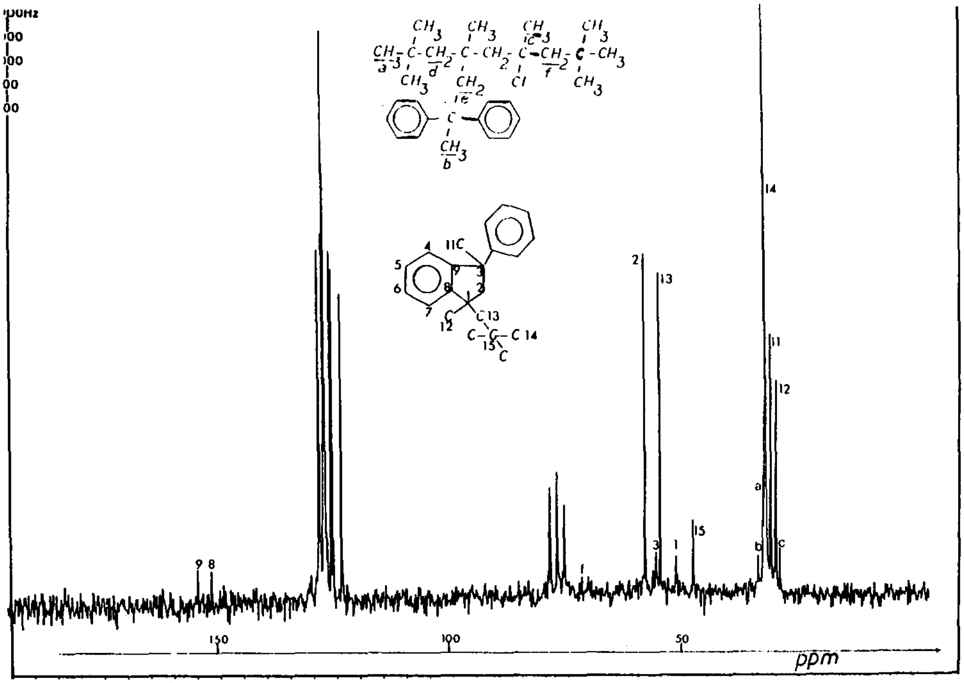
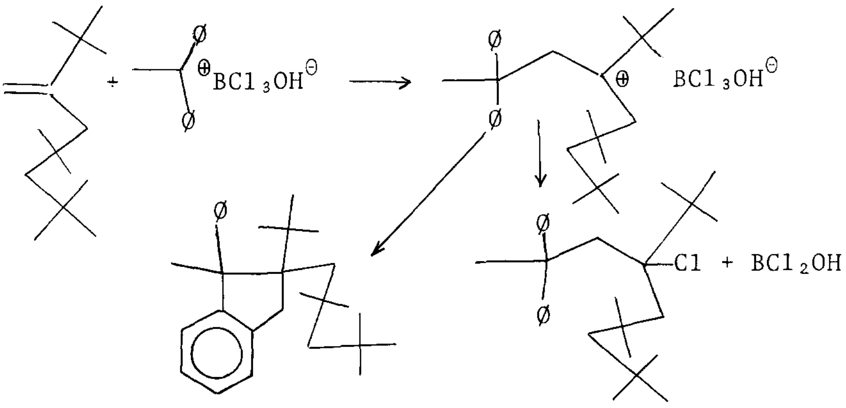


Figure V: ^{13}CMR spectrum of 1-neopentyl-1,3-dimethyl-3-indane + 4-chloro-2,2,4,6,8,8-hexamethyl-6(2',2'-diphenyl)-propylnonane

The proposition that TMP does not add to the intermediate carbenium ion in this system has been confirmed in independent experiments. In these studies mixtures of isobutylene tetramers were cationated by $C\emptyset_2C^{\oplus}BCl_3OH^{\ominus}$ and according to NMR analyses only those with exo unsaturation reacted:



(The ^{1}H NMR spectra obtained in an experiment in which a mixture of isobutylene tetramers were reacted with $C\emptyset_2COH/BCl_3$ and that in which TMP was reacting with the same combination, were almost identical.) The fact that chlorinated product is formed with isobutylene tetramers but not with TMP may be due to the reduced rate on intramolecular alkylation on account of steric compression in the former system. Thus, the collapse of the ion pair (by chlorine transfer from the counter anion to the carbenium center) is relatively more important in the isobutylene system than with TMP.

References

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Accepted October 28, 1981