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Cationic Oligomerization and Copolymerization with Styrene of 2,3-Diphenyl-1,3-Butadiene by P-Dicumylchloride/Lewis Acid and "H₂O"/Lewis Acid Systems

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**CATIONIC OLIGOMERIZATION AND
COPOLYMERIZATION WITH STYRENE OF
2,3-DIPHENYL-1,3-BUTADIENE BY
p-DICUMYLCHLORIDE/LEWIS ACID AND
“H₂O”/LEWIS ACID SYSTEMS**

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ABSTRACT

Homo and copolymerization with styrene of 2,3-diphenyl-1,3-butadiene (DPBD) were investigated in the presence of a variety of Lewis acids (LA) such as TiCl₄, BCl₃, AlCl₃, and SnCl₄. In the presence of “H₂O” and 1,4-bis(2-chloro-2-propyl)benzene (p-dicumylchloride, p-DCC) initiators predominantly “unimers” and dimers are formed. The copolymerization of DPBD with styrene was achieved with the DPBD/Sty/p-DCC/Pyridine/TiCl₄ system. Pure copolymer was obtained by fractional precipitation. The composition of the copolymer was determined by ¹H-NMR spectroscopy.

INTRODUCTION

In the course of our studies on cationic olefin polymerization [1, 2] we became interested in exploring the cationic polymerization of DPBD to obtain irregular structural units in a polystyrene chain deliberately. A thorough literature

search yielded some data [3] on cationic polymerization of DPBD, and no data for the cationic copolymerization of styrene and DPBD.

Similar dienes, e.g., 2,3-dimethyl-1,3-butadiene, have been reported to be "poisonous" in cationic polymerizations [4]. The free radical homopolymerization of DPBD gave after reduction exclusively head-to-head poly(styrene) [5]. A free radical copolymerization, was also successful [6]. Against this background our purpose was to investigate the cationic homo- and copolymerization of DPBD in the presence various Lewis acids.

MATERIALS

p-DCC was prepared from 1,4-bis(2-hydroxy-2-propyl) benzene in CH_2Cl_2 as described earlier [1]. Methylcyclohexane (MCH) (Aldrich) was distilled over CaH_2 and CH_2Cl_2 (Aldrich) was distilled over P_4O_{10} . Styrene was extracted with sodium hydroxide solution, washed with water, dried over CaH_2 , and distilled under reduced pressure prior to use. Pyridine (Reanal) was distilled over potassium hydroxide. TiCl_4 (Merck) and SnCl_4 (Reanal) were distilled under a nitrogen atmosphere. DPBD (Fluka), AlCl_3 (Ferak, Berlin), BCl_3 (Merck) and methanol (Reanal) were used as received.

METHODS

Synthesis of homopolymer: The polymerization was carried out in a 50 mL test-tube in a dry-box, at -80°C under a dry nitrogen atmosphere. 5×10^{-5} mole (0.0155 g) p-DCC, and 1.2×10^{-3} mole (0.25 g) DPBD were dissolved in CH_2Cl_2 . The volume of the solution was 10 mL. The polymerization was started by adding 1.5×10^{-3} mole coinitiator (see Table 1) to the charges. The polymerization was terminated with 2 ml of prechilled methanol after 120 minutes.

Synthesis of copolymer: 5×10^{-5} mole (0.01155 g) p-DCC, the two monomers (see Table 2) and 1.0×10^{-4} mole (0.008 ml) pyridine were dissolved in a mixture

Table 1

Conditions and results of polymerization of DPBD

([p-DCC]= 5×10^{-5} mole; [coinitiator]= 1.5×10^{-3} mole; [DPBD]= 1.2×10^{-3} moleT = -80 °C; t = 2 hours; CH₂Cl₂)

Initiator	Coinitiator	Conv. %	Remarks and results
"H ₂ O"	TiCl ₄	74	only oligomers
"H ₂ O"	BCl ₃	7	oligomers and traces of polymers
"H ₂ O"	AlCl ₃	50	only oligomers
"H ₂ O"	SnCl ₄	<1	no polymerization
p-DCC	TiCl ₄	69	only oligomers
p-DCC	BCl ₃	27	oligomers and traces of polymers
p-DCC	AlCl ₃	74	only oligomers
p-DCC	SnCl ₄	79	oligomers and traces of polymers

of methylcyclohexane/CH₂Cl₂ (60/40 v/v). The volume of the solution was 25 mL. The polymerization was started by adding 1.0×10^{-3} mole (0.43 ml) TiCl₄ at -80 °C and was stopped with 2 mL of prechilled methanol after 120 mins. Polymers were purified by precipitation with methanol.

Characterization methods: Size-Exclusion Chromatography (SEC) and ¹H-NMR measurements have been published earlier [1]. A series of polystyrene standards were used for the calibration of SEC.

RESULTS AND DISCUSSION

Homopolymerization

Initiation of homopolymerization of DPBD was carried out in the presence of a variety of Lewis acids. Results and conditions are summarized in Table 1.

A comparison of conversions obtained in the presence of “H₂O”/LA and p-DCC/LA initiating systems shows a significant increase in conversion, indicating the initiating activity of p-DCC. In the presence of TiCl₄ and AlCl₃ only low molecular mass oligomers are formed. According to our SEC results (We calculated the M_n values from SEC traces using a series of polystyrene standards.), the highest degree of polymerization is 2. The amount of polymer formed with “H₂O”/BCl₃, p-DCC/BCl₃ and p-DCC/SnCl₄ are detectable only by SEC. The major products in these cases are “unimers”, i.e., the reaction product between the initiator and the first monomer unit, and dimer. Figure 1. shows the representative SEC traces.

The SEC trace indicates that after ion generation one monomer unit is incorporated. After ionization of the second initiator site, reaction with the second monomer yields dimer. The dimer is unable to propagate. A possible explanation for this behavior may be that after the first crossover, the cumyl cation is transformed to a highly stabilized carbenium ion (Scheme 1, I stands for the initiator moiety).

We cannot exclude the possibility of intramolecular alkylation/deprotonation resulting in indenyl skeleton formation, a frequent process in cationic polymerization of styrene and its derivatives [4] (Scheme 2).

Copolymerization with styrene

The copolymerization experiments we designed to show whether the highly stabilized chain end is capable for crossover with a more reactive second monomer. The model was the DPBD/Styrene system. Conditions are summarized in Table 2.

No copolymers formed in the presence of BCl₃ coinitiator. A mixture of copolymers and oligomers were obtained with the p-DCC/pyridine/TiCl₄ initiating system.(Figure 2).

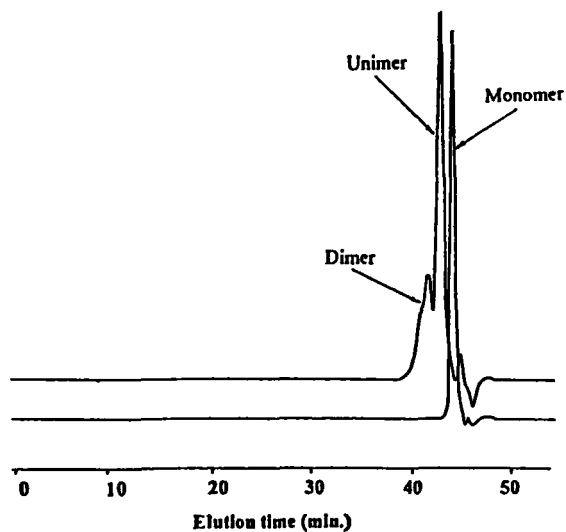
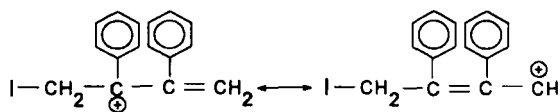
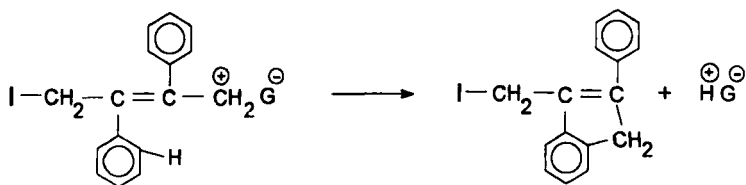


Figure 1. The SEC traces of oligomers obtained by p-DCC/TiCl₄ initiating system (The calibration was made by a series of polystyrene standards)



Scheme 1



Scheme 2

Intramolecular ring formation

Table 2

Conditions for the Copolymerization of DPBD with Styrene

([p-DCC] = 5×10^{-5} mole; [TiCl₄] = 1×10^{-3} mole; [Pyridine] = 1×10^{-4} mole
CH₂Cl₂ : MCH = 2:3, T = -80 °C, t = 2 hours, Pyridine was used to obtain living
polymerization of styrene [7].)

DPBD		Styrene		DPBD/Sty	Conversion
g	mmole	g	mmole	mole/mole	%
0.05	0.242	0.45	4.321	0.056	100
0.10	0.485	0.40	3.841	0.13	100
0.25	1.212	0.25	2.400	0.51	88
0.35	1.697	0.15	1.440	1.18	83
0.45	2.181	0.05	0.480	4.54	75

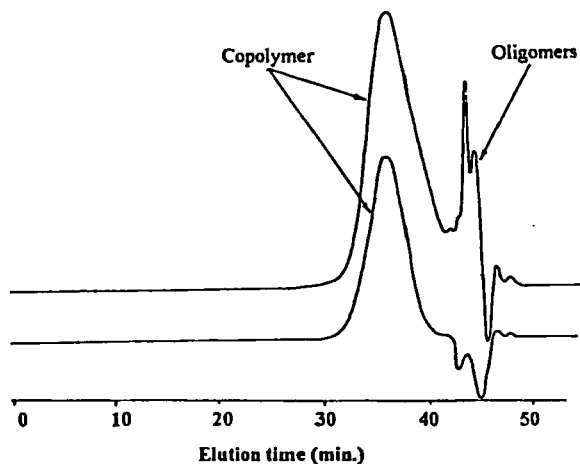


Figure 2. Representative SEC traces of the crude and fractionated pure copolymer (Conditions are in Table 2, second row)

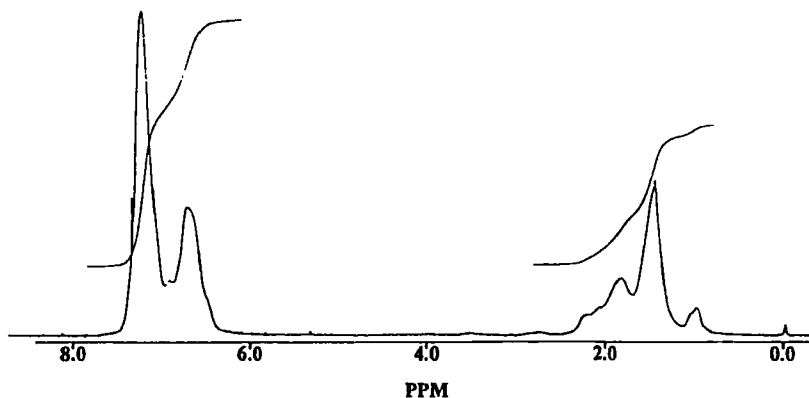


Figure 3. $^1\text{H-NMR}$ spectrum of copolymer

Because of the large difference in molecular mass of oligomers and polymers, we were able to separate the polymers of higher molar mass from the oligomers by fractional precipitation. (The crude polymer was dissolved in dichloromethane and precipitated by methanol.) In this way 5.7 percent of pure copolymer was obtained (Fig. 2.). From the $^1\text{H-NMR}$ spectrum (Fig. 3.) of the copolymer, we calculated the ratio of monomers in the pure copolymer as follows:

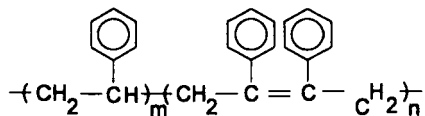
$$\bar{M}_n = 104 \cdot N_{\text{St}} + 206 \cdot N_{\text{DPBD}} + 231$$

$$\frac{I_{\text{arom}}}{I_{\text{aliph}}} = \frac{5 \cdot N_{\text{St}} + 10 \cdot N_{\text{DPBD}} + 4}{3 \cdot N_{\text{St}} + 4 \cdot N_{\text{DPBD}} + 12}$$

where I_{arom} = integration value of aromatic protons, I_{aliph} = integration value of aliphatic protons, N_{St} = number of styrene units, N_{DPBD} = number of DPBD units, 4 = number of aromatic protons of initiator moiety, 12 = number of aliphatic protons of initiator moiety

According to this equation-system, and considering $\bar{M}_n=3900$ g/mole and $I_{\text{arom}}/I_{\text{aliph}}=1.75$ (MWD=1.63), the copolymer contains 20.5 styrene and 7.4 DPBD units. The $^1\text{H-NMR}$ spectrum shows no olefinic protons within

the experimental error, indicating a regular 1,4 enchainment of DPBD after the cross-over. Thus, the structure of the copolymer is as follows:



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