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Attempted cationic polymerization of isosafrole

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Summary

The cationic polymerization/oligomerization of [1,2-(methylenedioxy)-4-propenyl benzene] (isosafrole), was conducted under a variety of conditions. When products were obtained they proved to be very low molecular weight materials (DP = 3-8). The reaction temperature and/or the presence or absence of solvent had the most significant impact on product yield and molecular weight. In most cases polymerization proceeded through the propenyl group, although at higher reaction temperatures there was evidence of reaction with the methylenedioxy group.

Introduction

There have been several reports in the literature concerning the attempted cationic polymerization of isosafrole (1-4). However, these reports contain very few details concerning the conditions employed or the nature of the products obtained. Therefore, we decided to investigate the cationic reactivity of isosafrole under a variety of conditions. This paper summarizes the preliminary results we obtained.

Experimental

General

All solvents used in this study were reagent grade and were distilled from the appropriate drying agent before use. The isosafrole (Aldrich) was purified by distilling from CaH_2 three times. All initiators were obtained in 99+% purity (Aldrich) and were used as received. ^{1}H-NMR spectra were obtained at 90 MHz with a Perkin-Elmer R-32B instrument operating in the CW mode and at 300 MHz with a Varian Gemini 300 FT NMR. All spectra were recorded at ambient temperature on 10-15% w/v solutions in $CDCl_3$. Molecular weights were measured with a Waters 150 ALC/GPC equipped with 10^6,

10^5, 10^4, 10^3, 500 and 100 Å microstyragel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Polymer Synthesis

Bulk polymerizations were performed by charging isosafrole (7.0 g) to a clean, dry test tube (15 ml) equipped with a magnetic stirring bar. The isosafrole was sparged with and the tube flushed with, dry N_2. The tube was sealed with a rubber septum and placed in a fluid bath at the desired temperature. The contents of the tube were allowed to equilibrate (~15 min) and the initiator was added via syringe if it was liquid. If the initiator was solid it was added to the tube by briefly removing the septum, under a flow of N_2, and rapidly pouring the initiator into the vigorously stirred contents of the tube.

For the solution polymerizations, monomer (7.0 g) was charged into a 20 ml test tube equipped as above, and the solution was sparged with dry N_2. The tube was flushed with N_2 and sealed with a rubber septum. The solution was placed in a fluid bath at the desired temperature and was allowed to equilibrate for 15 min. The initiators were added as described for the bulk polymerization.

The only exception to these procedures was the $AlCl_3/SbCl_3$ initiator system. When this initiator system was used the $SbCl_3$ was added last, via syringe, dissolved in either the polymerization solvent or a small amount of monomer.

In all cases, the polymerizations were terminated by the injection of 5 ml of cold CH_3OH. Any solid material was dissolved in $CHCl_3$ and precipitated by addition to 8-10 fold excesses of CH_3OH. The solid material was purified by reprecipitating twice from $CHCl_3$ solution into excess CH_3OH. All solid materials were collected by filtration and dried in vacuo at 30°C for 72 h. Yields were determined gravimetrically.

Results and Discussion

The conditions employed and the results obtained are summarized in Table 1. Nearly all the materials produced, in reactions where product could be isolated, are oligomeric with DP's = 3-8. The data shows that DP's are independent of the initiator used, however the initiator does somewhat influence the yield of product obtained. Note that all the results presented in Table 1 are the average of two experiments performed under the conditions listed. The lowest yields of CH_3OH insoluble products were obtained with the mostly insoluble initiators such as $AlCl_3$ or $AlCl_3/SbCl_3$. The $AlCl_3/SbCl_3$ initiator system has been reported (5-7) to give higher yields and higher molecular weights than any previously obtained in the polymerization of α- and β-pinenes. However, in the present case, conducting the polymerization of isosafrole with this initiator system under the conditions recommended by Higashimura et al (7), yielded no methanol insoluble products. A small amount of dimer (∼5% conversion) was produced, but the great majority of recovered material, ∼92 wt % of the initial charge, was unreacted monomer. The data in Table 1 shows that any polymerization attempted in solvent yielded no methanol insoluble products regardless of the initiator used. This could be due to a high chain transfer to solvent constant; the polymerization of 1,2-disubstituted olefins is known to be slow (8) which could favor chain transfer reactions in the appropriate media. Presently, the data is insufficient to support this hypothesis in a quantitative fashion, but the results do suggest that some kind of transfer/termination mechanism is operating in solvent media.

The bulk polymerizations listed in Table 1 show the importance of reaction temperature. Polymerization temperatures of less than 5°C produce no polymeric/oligomeric species, while polymerization temperatures of 30°C and above show involvement of the dioxymethylene in the polymerization when certain initiators are used ($BF_3 \cdot OEt_2$) up to the point of producing crosslinked, insoluble materials (45°C). A reaction temperature range of 15-25°C seems to be optimum for control of the reaction and for the maximum yield of product to be obtained, however the reactions done at 30°C yield the highest molecular weight products.

Because reactions performed in solvent yielded no polymer regardless of initiator or temperature employed, initiation with the $AlCl_3/SbCl_3$ system was attempted in bulk at 20°C. Some polymer/oligomer was obtained (ISO 18) but not substantially more than was obtained with $AlCl_3$ was used by itself as the initiator, although a higher molecular weight material was obtained with the $AlCl_3/SbCl_3$ initiator.

The results presented in Table 1 also show that the M/I ratio has no effect on product yield or molecular weight.

Figure 1A shows the 90 MHz ^{1}H-NMR of the ISO 2 oligomer, all the signals are assigned as shown in the Figure (5,9). Clearly, the dioxymethylene group ($\delta = 5.70$) is present and, with the error limits of the electronic integration of the instrument (±2%), it is present in total i.e. there is no evidence of reaction. Figure 1B shows the 300 MHz ^{1}H-NMR spectrum of ISO 4. Clearly, the resonances due to the aromatic ring are much broader which is partly due to the higher molecular weight of ISO 4. But, given the greatly diminished resonance at $\delta = 5.90$, which can be assigned to the dioxymethylene group, is also partly due to participation of the ring in side reactions, possibly alkylation. Also, the GPC trace of ISO 4 shows multimodality, again indicating that side reactions take place, most probably through the dioxymethylene group. ^{13}C-NMR spectroscopy of ISO 4 and ISO 13 yielded spectra with a large number of signals, too many signals in fact for any reasonable interpretation to be made at this time. However, the presence of such a large amount of signals also indicates the participation of side reactions in this polymerization.

TABLE 1

Isosafrole Polymerization/Oligomerization Results

Polymer	Initiator	M/I	Polymerization Temperature °C	Polymerization Time (h)	Solvent	% Conv.	M_n	M_w	M_w/M_n
ISO 1	$BF_3 \cdot OEt_2$[a]	20	0	5.0	-	0	-	-	-
ISO 2	$BF_3 \cdot OEt_2$	20	20	5.0	-	25.3	870	1100	1.26
ISO 3	$BF_3 \cdot OEt_2$	20	20[b]	5.0	-	45.4	500	600	1.20
ISO 4	$BF_3 \cdot OEt_2$	20	30	1.5	-	85.0	4200	20500	4.88
ISO 5	$BF_3 \cdot OEt_2$	20	45	1.0	-	100	crosslinked product		-
ISO 6	$BF_3 \cdot OEt_2$	30	20	5.0	-	37.7	480	570	1.19
ISO 7	$BF_3 \cdot OEt_2$	40	-76	5.0	CH_2Cl_2	0	-	-	-
ISO 8	$BF_3 \cdot OEt_2$	40	0	5.0	-	0	-	-	-
ISO 9	$BF_3 \cdot OEt_2$	40	20	5.0	-	41.5	450	540	1.20
ISO 10	$BF_3 \cdot OEt_2$	40	20	3.0	CH_2Cl_2	0	-	-	-

TABLE 1

(Continued)

Polymer	Initiator	M/I	Polymerization Temperature °C	Polymerization Time (h)	Solvent	% Conv.	M_n	M_w	M_w/M_n
ISO 11	$BF_3 \cdot 2CH_3COOH$	20	20	5.0	-	34.3	500	650	1.30
ISO 12	$SnCl_4$	20	20	5.0	-	22.8	540	600	1.11
ISO 13	$SnCl_4$	20	30	1.5	-	80.0	1000	3000	3.00
ISO 14	$SbCl_4$	20	20	5.0	-	0	-	-	-
ISO 15	$AlCl_3$	20	20	5.0	-	5.75	560	630	1.13
ISO 16	$AlCl_3/SbCl_3$	20	0	5.0	Toluene	0	-	-	-
ISO 17	$AlCl_3/SbCl_3$	20	20	5.0	Toluene	0	-	-	-
ISO 18	$AlCl_3/SbCl_3$	20	20	5.0	-	6.2	700	970	1.39

a. $BF_3{:}OEt_2$ = Boron trifluoride etherate
b. Reaction performed with highly purified (distilled 5x's) isosafrole

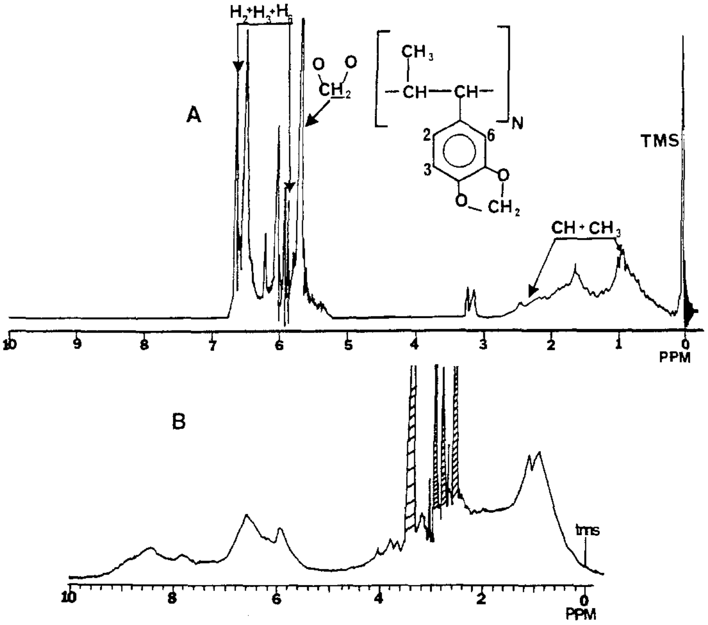

Figure 1

A) 90 MHz ^{1}H-NMR Spectrum of ISO 2;

B) 300 MHz ^{1}H-NMR Spectrum of ISO 4

Conclusions

The polymerization of isosafrole under a variety of conditions was attempted. The major factors affecting the course of the reaction are the presence or absence of solvent and temperature. Reactions conducted in solvent yield no polymeric/oligomeric products. Reactions conducted below 10°C also yield no polymeric/oligomeric products. Reactions conducted at 30°C and above yield the highest molecular weight materials but also give partially or totally crosslinked products due to participation of the dioxymethylene group in the reaction. The type of Lewis acid and the monomer/initiator ratio had very little effect on the reaction, with the exception that liquid initiators, which were far more soluble, gave greater yields of product.

In general, all soluble products were bright white powders that had very low molecular weights. It is suspected that these low molecular weights reflect the generally sluggish polymerization behavior of 1,2-disubstituted ethylenes, which provides opportunities for chain transfer possibly through the dioxymethylene group.

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