

New Catalysts for the Polymerization of Diisopropenylbenzenes

A. A. D'ONOFRIO, *Research and Development Department, Union Carbide Plastics Company, Division of Union Carbide Corporation, Bound Brook, New Jersey*

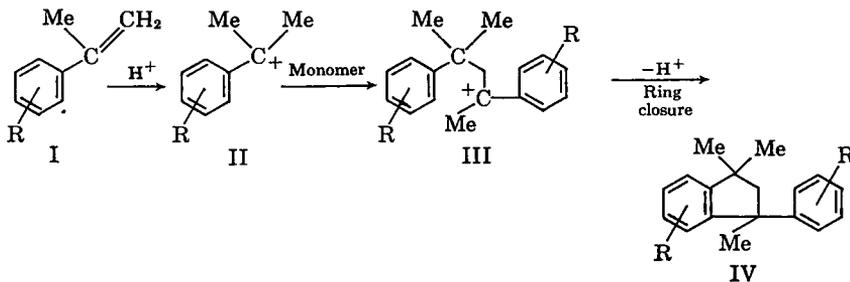
Synopsis

Linear, high molecular weight, soluble, catalyst-free polyindanes have been prepared by the polymerization of *p*-diisopropenylbenzene with a series of insoluble complex catalysts. A new synthesis of *p*-diisopropenylbenzene is reported.

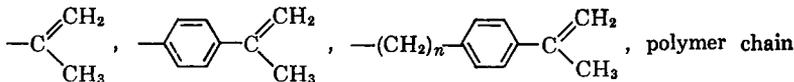
Introduction

The solution polymerization of diisopropenylbenzenes and their homologues to yield linear, soluble polyindanes has been described recently.¹⁻⁶ In all of these examples, Lewis acid-type catalysts were used, and a polymerization mechanism^{1,2,7,8} analogous to that for the acid-catalyzed dimerization of α -methylstyrene was advanced:

where R may be



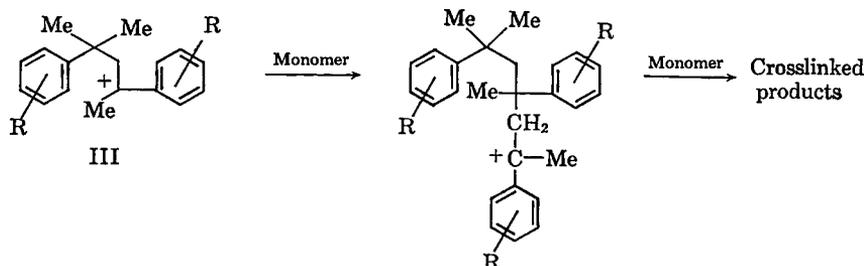
where R may be



Discussion

During our work on the polymerization of diisopropenylbenzene monomers it became apparent that the use of Lewis acid catalysts (BF_3 , TiCl_4 , SnCl_4 , etc.) had the following rather serious shortcomings:

(1) A narrow, elevated polymerization temperature range (70–100°C.) was necessary in order that soluble polymer be obtained. At temperatures lower than 70°C. monomer added to structure III before ring closure, and crosslinked products resulted.²

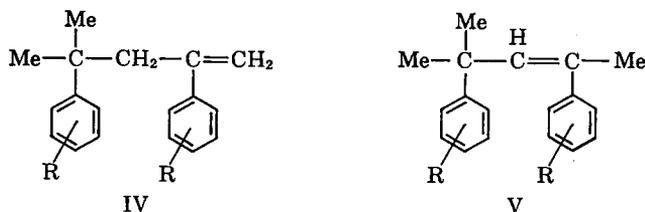


At temperatures higher than 100°C. the activity of the catalyst decreased.

(2) Long reaction times⁴⁻⁸ were necessary in order to obtain high molecular weight polymers (40–100 hr.).

(3) The soluble catalyst residues were difficult to remove from the polymers.

(4) Except in quite critical ranges of monomer and catalyst concentration and temperature, the resulting polymers contained a relatively large proportion of olefinic unsaturation² due to the incorporation of 4-aryl-4-methylpentene-1 and 2 (IV, V) moieties in the polymer chain.



In a recent publication⁹ Evans and Owen described the quantitative dimerization of 1,1-diphenylethylene (VI) to 1,1,3-triphenyl-3-methylindane (VII) in benzene, using the complex catalyst system, LiBu-TiCl₄-HCl, (Li/Ti mole ratio = 1.3)



The use of this insoluble complex catalyst (at a Li/Ti mole ratio of 1.0–2.0) for the polymerization of diisopropenylbenzenes afforded linear

polyindanes nearly identical in properties to those prepared with Lewis acid catalysts. However, certain advantages ensued with the use of the LiBu-TiCl₄-HCl complex system: (1) soluble polymers were obtained over a broader polymerization temperature range (0-130°C.); (2) the insoluble catalyst residues were easily removed from the soluble polymers by filtration; (3) high molecular weight polymers were obtained in much shorter times (0.5-20 hr.); (4) the ring closure was quantitative and was independent of catalyst concentration over the broad range studied and the polymers contained no olefinic unsaturation other than terminal.

In addition to the LiBu-TiCl₄-HCl system, it was found that a number of Ziegler-type complexes in combination with HCl at Al/Ti mole ratios of 1.0-2.0 gave soluble, high molecular weight polyindanes from the diisopropenylbenzenes. Some examples of these are given in Table I, which lists the metal/titanium mole ratio which gave soluble polyindanes. That these complexes were truly catalytic was convincingly demonstrated in all cases. For example, omission of the HCl in the LiBu-TiCl₄-HCl system, (Li/Ti ratio = 1.5), resulted in no polymerization even after 100 hr. at 25°C. If TiCl₄-HCl was used alone at 25°C., the product after 24 hr. was 45% toluene-insoluble (gel), with the soluble portion containing internal olefinic unsaturation. With LiBu-HCl no polymerization took place after 24 hr. at 25°C. However, when the LiBu-TiCl₄-HCl complex (Li/Ti ratio = 1.5) was used at 25°C. then an essentially quantitative yield of high molecular weight, soluble polymer containing no internal olefinic unsaturation was the result.

A more detailed account of these complex catalysts is the subject of a pending U.S. patent application.

Experimental

The following is an example of the standard procedure used for the polymerization of *p*-diisopropenylbenzene.

Dry toluene (100 ml.) and 0.0702 g. TiCl₄ (3.7×10^{-4} moles) were charged under nitrogen to a dry 250-ml. flask. This was rapidly stirred while 0.216 ml. of a 14.8% solution of butyllithium (4.9×10^{-4} moles) in 33/66 pentane-heptane was added. An insoluble, finely divided brown-black complex was formed. A slow stream of gaseous HCl was admixed with the incoming nitrogen and the flask immersed in a constant temperature bath held at 25°C. A solution of 13.0 g. of *p*-diisopropenylbenzene in 30 ml. of dry toluene was added dropwise over a period of 15 min. The mixture was stirred for 20 hr. in the nitrogen-HCl atmosphere. The viscous mass was then diluted with 200 ml. of toluene, filtered to remove the insoluble catalyst residues, and coagulated in ethanol. The precipitated polymer was filtered and then dried at 80°C. and 20 mm. Hg for 8 hr. The yield was 12.1 g., reduced viscosity = 0.81 (measured in benzene at 25°C. at a concentration of 0.2 g./100 ml.). The polymer had a softening point of 280-290°C. and a degree of unsaturation of less than 0.05% as measured by the Hanus IBr test.¹⁰

TABLE I
Polymerization of *p*-Disopropenylbenzene

Expt.	Catalyst	Metal titanium mole ratio	Catalyst mole/mole monomer	Mono-mer concn. in toluene, %	Poly-meriza- tion time, hr.	Poly-meriza- tion temp., °C.	Yield toluene-insoluble polymer, %	Yield toluene-soluble polymer, %	Reduced viscosity of soluble polymer ^a	Softening point, °C. ^b	C=C, % ^c
1	LiBu-TiCl ₄ -HCl	1.32	0.004	10	20	25	0	93	0.81	280-290	<0.05
2	LiBu-TiCl ₄ -HCl	1.50	0.004	10	4	100	0	88	0.30	271-281	0.07
3	LiBu-TiCl ₄ -HCl	0.85	0.004	10	20	25	40	40	0.24	260-272	0.28
4	LiBu-TiCl ₄ -HCl	1.2	0.04	10	20	25	0	90	0.31	268-274	<0.05
5	LiBu-TiCl ₄ -HCl	1.2	0.004	50	20	25	13	81	0.55	275-278	0.17
6	Al(Et) ₃ Ti(OBu) ₄ -HCl	1.5	0.004	10	10	25	0	96	0.75	278-289	<0.05
7	Al(<i>i</i> -Pr) ₃ Ti(OBu) ₄ -HCl	1.5	0.004	10	4	0	0	92	0.41	271-277	0.08
8	Al(<i>i</i> -Pr) ₃ Ti(OBu) ₄ -HCl	3.5	0.004	10	5	25	80	10	0.07	—	—

^a Reduced viscosities were measured in benzene at 25°C., at a concentration of 0.2 g./100 ml.

^b Softening points are uncorrected and were measured on a Leitz Microscope Heating Stage 350.

^c Analysis for unsaturation was done by the Hanus IBr method.

Diisopropenylbenzene was previously reported by Bogert,¹¹ who obtained 1,4-di-(hydroxyisopropyl)benzene (II) from the Grignard reaction of dimethyl terephthalate and methylmagnesium iodide. Dehydration of II with potassium bisulfate gave I. However, this synthesis proved cumbersome and inefficient in our hands, resulting in overall yields of only 20–40%.

We wish to report a modified Wittig procedure whereby *p*-diisopropenylbenzene can be readily prepared in yields of 85–90% by the reaction of 1,4-diacetylbenzene with methylenetriphenylphosphorane in dimethoxyethane.

A mixture of 109.8 g. of methyltriphenylphosphonium bromide, 310 cc. of dry dimethoxyethane, and 7.2 g. of finely ground sodium hydride was agitated for 3 hr. in order to generate methylene-triphenylphosphorane. To this suspension was added 18.0 g. of *p*-diacetylbenzene dissolved in 200 cc. of dry dimethoxyethane, and the suspension was allowed to reflux for 3 hr. and then cooled. To this mixture was added 400 cc. of distilled water and 140 cc. of diethyl ether. The water layer was separated and discarded. The ether and dimethoxyethane were evaporated under vacuum, leaving a residue of triphenylphosphine oxide and *p*-diisopropenylbenzene which solidified on cooling. This residue was triturated three times with 200 cc. of heptane, and the heptane solution was evaporated under vacuum to yield a solid residue. This solid was recrystallized from a 3/1 ethanol-water mixture and yielded 15.6 g. (92%) of *p*-diisopropenylbenzene (white flakes), m.p. 63.5–64.5° (lit.¹) 63.6–64.0°C. The infrared spectra of this product was identical to the product prepared by the Bogert procedure. As was shown with α -methylstyrene,¹² *p*-diisopropenylbenzene shows a small but definite tendency to polymerize in storage and was kept in a brown bottle under a nitrogen atmosphere.

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Résumé

On a préparé des polyindanes linéaires, de haut poids moléculaire, solubles et libres de catalyseur par polymérisation de *p*-diisopropénylbenzène avec une série de catalyseurs complexes insolubles. On rapporte une nouvelle synthèse de *p*-diisopropénylbenzène.

Zusammenfassung

Lineare, hochmolekulare, lösliche, katalysatorfreie Polyindane wurden durch Polymerisation von *p*-Diisopropenylbenzol mit einer Reihe unlöslicher Komplexkatalysatoren dargestellt. Eine neue Synthese für *p*-Diisopropenylbenzol wird beschrieben.

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