

Technology Section

Pakistan J. Sci. Ind. Res., Vol. 24, Nos 5-6, October - December 1981

TURPENTINE OIL-BASED CHEMICALS

Part. III. Polymerisation of 3-Carene and α -Pinene

A. Sattar, M. Javaid Iqbal, K.M. Janjua, S.A Khan and M.K. Bhattu

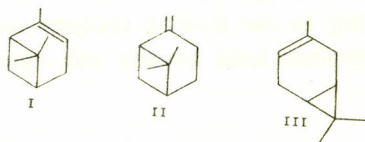
Oils, Fats and Waxes Research Division, PCSIR Laboratories, Lahore

(Received October 12, 1980)

Thermoplastic resins of varying softening points and molecular weights have been obtained from the cationically initiated polymerisation of 3-carene and α -pinene. Reaction conditions for the exothermic polymerisation with lewis acid catalysts have been studied and described.

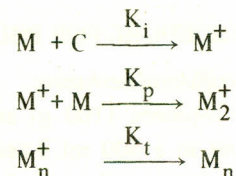
INTRODUCTION

The Pakistani turpentine [1] oil mainly consists of α -pinene (I, 35%), β -pinene (II, 15%) and 3-carene (III, 47%). Previously the use of this oil for the preparation of terpin hydrate [2], terpineol [3] and cymene [4] have been reported as part I and Part II of the series of publications on the turpentine oil-based chemicals. In continuation of our earlier work, we now have studied the utilisation of the monoterpenes occurring in the oil for the production of terpene resins. These resins ranging from viscous liquids to solids and having softening points up to 75^o, can find use in adhesives and adhesive compositions, varnishes and coatings.



The first recorded resinification of turpentine oil with sulphuric acid was carried out in 1789. Ever since this polymerisation process has been exhaustively studied. The monoterpenes undergo cationic polymerisation and do not follow the generally employed radical initiated polymerisations. This is exemplified by the fact that when dipentene and α -pinene were heated at 60-100^o for 100 hours with organic radical initiators such as benzoyl peroxide and azobis(isobutyryl peroxide), these terpenes did not polymerise at all [5]. Although cationic polymerisation is one of the oldest branches of polymerisation, yet opinion regarding its propagation is divided. However, it is generally accepted that in true cationic polymerisation, the propa-

gating ends carry positive charge. Schematically this polymerisation can be represented as:



where M and C indicate monomer and catalyst and M⁺, the propagating centre, K_i, K_p, and K_t indicates the initiation, propagation and termination rate constants.

Resinification of turpentine oil and monoterpenes present in the oil has been described in the patent literature [6-9]. It has been suggested that the conversion of α -pinene to β -pinene is the first step of this polymerisation process [10]. From comparative studies it has also been concluded that under identical conditions polymerisation of β -pinene is faster than of α -pinene.

EXPERIMENTAL

All extracts were dried over anhydrous sodium sulphate.

Toluene. Commercial grade toluene was purified by shaking it with conc. H₂SO₄, sodium hydroxide solution (10%) and water successively. Fractional distillation of the dried toluene gave middle fraction (boiling point 110-111^o) that was free from impurities when checked by GLC.

3-Carene and α -pinene. The locally available grade I turpentine oil having composition; α -pinene 35 %, β -pinene 15 %, and 3-carene 47 %, was fractionally distilled in a 5-litre flask (reboiler) equipped with a rectifying wire-gauge

plate column, a condenser and a receiver. The specifications of the rectifying glass column were as under:

Internal dia	=	25 mm
Height	=	122 cm
Wire gauze	=	60 mesh
Material of construction	=	Stainless steel
Number of plates	=	16

Trap tubes were fitted in the wire gauze plates in order to avoid flooding of the column and the proper maintenance of the plate efficiency. The reflux ratio was adjusted through the change in the heating rate of the reboiler flask. Pure α -pinene (95 %) and 3-carene (97 %) were obtained after repeated fractionation on this column. Boron trifluoride-etherate and anhydrous aluminium chloride supplied by E. Merck and BDH respectively were used as such without further purification.

GENERAL PROCEDURE FOR POLYMERISATION

i. *With Boron-trifluoride-etherate.* Terpene hydrocarbon, 3-carene or α -pinene (100 g) and purified toluene (80 ml) were taken in a 500 ml 3-necked flask equipped with a stirrer, a condenser with a guard tube and a dropping funnel. The required amount of boron trifluoride-etherate (3–11 %) in 20 ml of toluene was placed in the dropping funnel and was added to the reaction flask drop by drop. The reaction was exothermic and the addition of the catalyst was so regulated that the temperature did not rise beyond 30–35°. After the addition of the catalyst was complete, the reaction flask was placed in a thermostatically controlled bath and the mixture was stirred for 6 hours at the required temperature. The reaction product was cooled and 200 ml of toluene was added. The diluted product was neutralised with 5 % solution of sodium carbonate, washed twice with water and then dried. Removal of toluene on a rotary evaporator gave a brown viscous liquid which was distilled under a vacuum of 4 mm of Hg and the distillate, mostly monomer and dimer, was collected up to 200°. The residue was poured in a flat tray to solidify while it was still hot

ii. *With Anhydrous Aluminium Chloride.* To a mixture of terpene hydrocarbon (100 g) in purified toluene (100 ml) was added solid anhydrous aluminium chloride catalyst (3–11 %) little at time from the weighing bottle by removing the stopper of the reaction flask. The addition was regulated so as to maintain the temperature of the reaction mixture around 30–35°. The flask was then heated at the required temperature for 6 hours. The work-up of the reaction product was the same as in (i) above for BF_3 -etherate catalyst.

Molecular Weight Determination. The molecular weights of the polymers obtained from 3-carene and α -pinene with BF_3 -etherate and anhydrous AlCl_3 catalysts were estimated by viscosity measurements in the capillary viscometer of Ostwald's type. The measurements of dilute solution viscosities were made by comparing the efflux time (t) needed for a given volume of polymer solution in purified toluene to flow through the capillary tube of the viscometer with the corresponding efflux time (t_0) for the solvent toluene. The viscosity number (η_{sp}/C) was calculated by using the equation.

$$\eta_{sp}/C = \frac{t - t_0}{t_0}$$

The viscosity numbers of five different concentrations of each of the polymer were determined. A graph between the viscosity number for solution of different concentrations versus the concentration (g/100 ml) was plotted which gave a straight line. From the slope of the graph the value of the limiting viscosity number (η) was determined.

Solutions of varying concentrations of known molecular weights of polyglycols (M. wt. 400 and M. wt. 1000) were also prepared. The efflux time (t) of each concentration were found out with the help of the same viscometer at the same temperature. The limiting viscosity number (η) of both the polyglycols were also determined by the above procedure. A graph was plotted between the molecular weights and limiting viscosity number (η) of these polyglycols. From the graph the value of molecular weight corresponding to the limiting viscosity number for each polymer obtained from 3-carene and α -pinene was found out.

RESULTS AND DISCUSSION

The polymerisation of monoterpenes is a cationically initiated reaction and the catalysts generally employed are lewis acids; among these anhydrous AlCl_3 and BF_3 -etherate are frequently used.

Turpenetene oil grade I available in the local market was fractionally distilled on a rectifying column designed and developed in these Laboratories. It was a wide bore glass column inside of which 16 plates made of stainless steel wire gauze were constructed. The wire was provided by trap tubes made of glass and the distillation was controlled through the heating of the reboiler. The 3-carene and α -pinene got enriched on each distillation and the process had to be repeated three times to get sufficiently pure monoterpenes. β -pinene, however, could not be ob-

Table 1. Effect of temperature with 7% catalyst on the softening point and percent yield of the resins from 3-carene and α -pinene.

Temperature	Monomer	Catalyst	Percent yield of higher polymer	Softening point
35°	α -Pinene	A	35	63°
		B	30	60°
	3-Carene	A	20	Viscous resin
		B	18	Viscous resin
50°	α -Pinene	A	47	68°
		B	55	75°
	3-Carene	A	45	Semi solid
		B	50	Semi solid
90°	α -pinene	A	28	60°
		B	41	65°
	3-Carene	A	25	Viscous resin
		B	35	Viscous resin

A denoted anhydrous AlCl_3 ; B denoted BF_3 -etherate

tained in pure form and therefore, its polymerisation was not attempted.

3-carene and α -pinene were separately polymerised with anhydrous AlCl_3 and BF_3 -etherate catalysts at different temperatures, the results are summarised in Table 1. Toluene was found to be the best solvent for the monomers, 3-carene and α -pinene as well as their polymerised products because these were completely soluble in this solvent and also because it was easily removed from the products without any noticeable adverse effects. Benzene instead of toluene as a solvent also gave identical results.

The addition of the catalyst to the terpene solution was exothermic. Therefore, the catalyst was added slowly and some time the reaction flask was externally cooled. The reaction mixture was heated from 30 to 90° for 6–8 hours in a thermostatically controlled bath. The catalyst was washed out with dilute sodium carbonate solution at the end of the reaction. Monomer and low polymeric material were removed under vacuum from the polymerised product and the residue was allowed to cool in an open tray. α -pinene gave solid residues while that from 3-carene were obtained either viscous liquids or semi-solids depending upon

the conditions of polymerisation.

In our hands, BF_3 -etherate gave better yields of resins than anhydrous AlCl_3 . However, AlCl_3 gave higher yields of resins around 30–35° while BF_3 -etherate was more effective at 50–55°. At higher temperatures (85–90°) copious fumes of HCl gas would come out of the reaction mixture with anhydrous AlCl_3 and the yields of resins dropped down. Therefore, the polymerisation was not attempted beyond this temperature. The higher temperature (90°) had little effect on the yields with BF_3 -etherate. The yields and the softening points of the resins obtained from α -pinene showed rise in their values as the amount of the catalyst was increased from 3 to 11 percent (Fig 1). In the case of 3-carene, the resins started becoming semi-solid from thick liquids as the amount of catalyst was increased beyond 7 percent. Usually the addition of the catalyst is carried out in one step in cationic polymerisation; but in our studies, the addition of the catalyst was stepwise. This means that after each new addition of the catalyst, new propagating centres were created or else the already terminated small polymer chains were initiated for the addition of new units of the monomer. This can be an example of a transfer reaction in polymerisation as sugges-

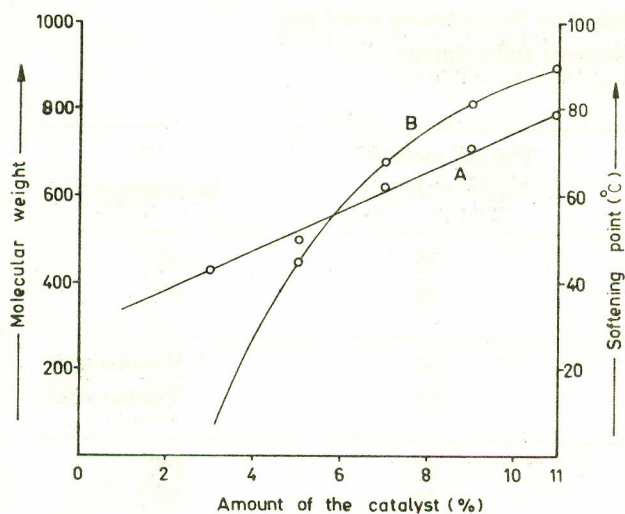


Fig. 1. Effect of the BF_3 -etherate catalyst on the polymerisation of α -pinene at 50° for 6 hours. (A) Percentage of the catalyst vs molecular weight. (B) Percentage of the catalyst vs softening point of the polymers.

ted by Flory [11]. According to him, for the increase or decrease in the growth of a polymer in vinyl polymerisation, transfer to monomer, transfer to polymer and transfer to solvent has a great effect without taking into account the number of active centres. This type of phenomenon is not common in cationic polymerisation and further research on this particular aspect need be carried out to trace out the mechanism of the growth of the polymer.

The molecular weights were estimated by viscosity measurements by comparison with polyglycols of known molecular weights. The molecular weights of the polymers obtained from α -pinene varied from 650–790 showing thereby that at least five repeating units of α -pinene are present in the polymer. 3-carene gave semi-solid polymers of molecular weights ranging from 550–560 proving thereby that 4 units of this terpene are incorporated in the product.

The low polymerisation of 3-carene compared to α -pinene can be ascribed to; a) the double bond, being

conjugated to the four-membered ring in α -pinene, initiates and stabilizes a cationic propagating centre for polymerisation better than that in 3-carene where the double bond is isolated; b) the propagating centre seems to be sterically more hindered in 3-carene than in α -pinene for the approach of another molecule. The propagating ion in β -pinene will be sterically less hindered and this will explain its higher yields.

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