

STUDY OF (ALUMINIUM CHLORIDE)/ α,α,α - BENZOTRICHLORIDE/TOLUENE HOMOGENEOUS INITIATING SYSTEM FOR THE POLYMERIZATION OF TURPENTINE

F. M. B. COUTINHO,* M. J. O. C. GUIMARÃES and A. L. N. SILVA

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, P.O. Box 68525,
21945 Rio de Janeiro, RJ, Brazil

(Received 10 October 1991)

Abstract—The efficiency of the initiating system (aluminium chloride)/ α,α,α -benzotrichloride/toluene for the polymerization of turpentine has been studied. The effects of the initiating system concentration, temperature and type of solvent on the polymerization conversion, molecular weight, molecular weight distribution and softening point of the resins were considered.

INTRODUCTION

Terpene resins are old, in fact the oldest reference to polymerization appeared in 1789 wherein turpentine was treated with sulphuric acid [1]. A later reference in a U.S. patent issued to Emile Rouxville in 1909 for subjecting hydrocarbons such as turpentine to sulphuric acid to produce a resin that resembled various India rubbers [2]. Twenty-four years later, aluminium chloride catalysis was patented for terpene polymerization by the Gulf Refining Company [3]. In 1950 fundamental publications employing Friedel-Crafts type catalysis [4, 5] referred to the polymerization of turpentine and pure terpenes such as β -pinene and dipentene (limonene) derived from turpentine by fractional distillation. Finally, the use of Ziegler-type catalyst to polymerize turpentine was reported by Achón [6, 7].

The attempts to polymerize turpentine were not very successful in producing resins with good properties and the resins did not possess potential commercial value, in contrast with the products from pure terpenes.

After the successful synthesis of aliphatic resins from C₃ petrol fraction by the use of a stable soluble catalyst complex obtained through the reaction of aluminium chloride and α,α,α -benzotrichloride in hydrocarbon medium [8], we became very interested in studying the polymerization of turpentine with that catalyst system.

EXPERIMENTAL PROCEDURES

Materials

Turpentine was twice distilled under reduced pressure over calcium hydride before use. Its composition, as determined by vapour-phase chromatography, was: α -pinene 54.7%; β -pinene 26.7%; myrcene 3.3%; limonene 8%; camphene 5.3%; and β -phellandrene 2%. α,α,α -Benzotrichloride was twice distilled under reduced pressure over CaH₂ and stored under dry N₂. Anhydrous aluminium

chloride was used as received. Toluene, benzene, xylene and methylene chloride were purified by the usual methods and twice distilled over CaH₂ just before use.

Polymerization procedure

The polymerizations were carried out under N₂ in a 250 ml flask equipped with stirrer bar and N₂ inlet and outlet. After purging the flask with dry N₂, the initiating system was prepared by adding sequentially AlCl₃ (coinitiator), toluene and α,α,α -benzotrichloride (initiator) in appropriate quantities. The reaction mixture was maintained at 25° for 20 min (period necessary to complete the solution of AlCl₃). Then solvent and monomer were added. Both the incremental monomer addition (IMA) and single monomer addition techniques were used. After a period at an appropriate temperature, the polymerization was terminated by addition of prechilled methanol and the resin was precipitated in an excess of methanol. The resin was purified by precipitating twice (CH₂Cl₂/CH₃OH), filtered off, washed with water and methanol and dried to constant weight. The resin conversion was gravimetrically determined. The molecular weights and molecular weight distributions of the resins were measured using a Toyo-Soda high pressure GPC equipped with three microstyragel columns. Molecular weights were based on a polystyrene calibration curve.

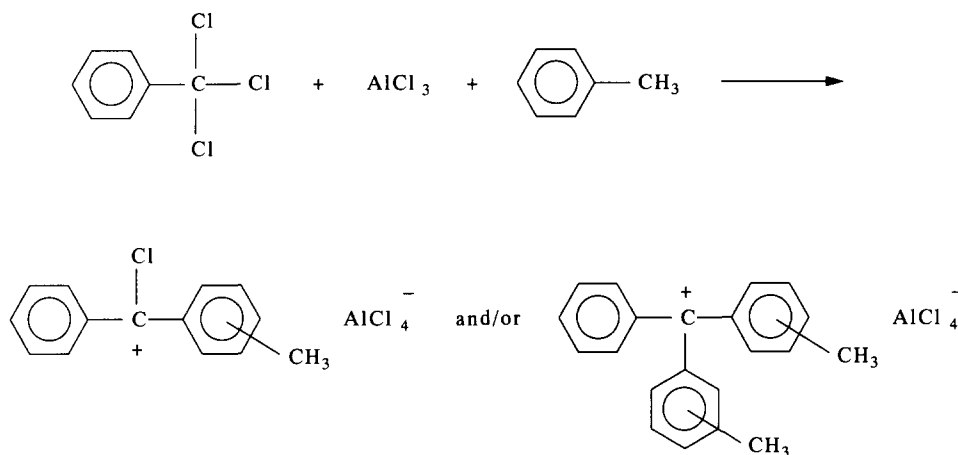
RESULTS AND DISCUSSION

The initiator consists of a complex formed from the Friedel-Crafts alkylation in which the role of aromatic diluent is essential to obtain a soluble system (Scheme 1).

In all experiments, the molar ratio of the components of the initiating system was fixed (1:1:10). The initiating mixture is dark red when fresh and changes to brown during aging, without loss of activity.

An increase in the initiating system concentration from 1 to 3% (based on monomer concentration) caused increase in the conversion from 32 to 60% and in the average molecular weight of the resin from 550 to 920; limiting values were reached (around 7%) and then decreases were observed. Excess of initiating system increased the termination of growing species by chain transfer [9]. A similar effect was observed

*To whom all correspondence should be addressed.



Scheme 1. Probable active species originating in the system $MCl_3/\phi-CCl_3/\phi-CH_3$ by Friedel-Crafts alkylation.

with variation of polymerization time. Resins varying in average molecular weight from 318 to 557 and polymerization conversion from 38 to 57% were obtained when the reaction time varied from 1 to 3 hr. The effect of temperature on the conversion was not significant but its influence on the molecular weight was. The average molecular weight and molecular weight distribution (expressed as \bar{M}_w/\bar{M}_n) varied directly with polymerization temperature from 667 to 776 and from 1.3 to 1.4 respectively at low temperatures ($-50-0^\circ$) and inversely from 776 to 550 and from 1.4 to 1.9 respectively at temperatures in the range of $0-35^\circ$.

The terpenes differ markedly in reactivity with decreasing temperature of polymerization [5]. As the polymerization involves a mixture of terpenes, the composition of resins must vary with the experimental conditions. In general, low temperature favours the polymerization of α -pinene which is the least reactive of the common terpenes for steric reasons. It is reasonable to believe that, when the temperature of polymerization is lower, the resin is richer in α -pinene. This view is confirmed by consideration of the softening point and the molecular weight distribution. At low temperatures ($-50-0^\circ$), resins varying in molecular weight distribution from 1.3 to 1.4 and softening point from 104 to 120° and at higher temperatures ($0-35^\circ$), variations in molecular weight distribution and softening point from 1.4 to 1.9 and from 104 to 108° respectively were obtained. It is known that, for a specified softening point, resins based on limonene and α -pinene have lower molecular weights than β -pinene resins, indicating that polymers of these terpenes are more rigid and more compact. They have a higher softening point and a narrower molecular weight distribution. In contrast, higher temperature of polymerization favours resins richer in β -pinene with wider molecular weight distribution and lower softening points.

The conversion and the molecular weight are decreased by chain transfer with aromatic solvents [10]. The effectiveness of methyl-substituted benzenes for chain transfer reached a maximum with dimethylbenzene (xylene). In methylene chloride, a more polar solvent, the growing species are more dissociated than in aromatic solvents and hence more susceptible to chain transfer to monomer.

Polymerization were also carried out in the absence of $\phi-CCl_3$ (heterogeneous system). In such experiments only *viscous liquids* were obtained for temperatures from 15 to 30° . The results show the low efficiency of $AlCl_3$ in the absence of $\phi-CCl_3$ to polymerize turpentine.

Acknowledgements—We thank Dr Antonio Mauricio de Fegueiredo (CENPES/PETROBRÁS) for providing α,α,α -benzotrichloride and CNPq, CAPES, FAPERJ and DIVEN/PETROBRÁS for financial support

REFERENCES

1. R. D. D. Watson. *Chem. Assays*, **III**, 5; MDCCLXXXIX (1789).
2. E. Rouxville. *U.S. Pat.* 919,248 (1909).
3. S. M. Cooper. Gulf Refining Co. *U.S. Pat.* 1,938,320 (1933).
4. S. I. Certkova, W. G. Plijuskif and E. P. Babin. *Zurn. prikl. chim. (J. Angew. Chem. Moskau Leningrad)* **29**, 1865 (1950).
5. W. J. Roberts and A. R. Day. *J. Am. chem. Soc.* **72**, 1226 (1950).
6. M. A. Achón, M. I. G. Banón and J. L. Mateo. *Makromolek. Chem.* **26**, 175 (1958).
7. M. A. Achón, M. I. G. Banón, J. L. Mateo and J. L. Ynfíest. *An. Fis. y Quím.* 1041 (1960).
8. A. M. Figueiredo, A. Malheiros and A. C. Teixeira. *Brazilian Pat.* 8304,576 (1985).
9. J. P. Kennedy and E. Maréchal. *Carbocationic Polymerization*. Wiley, New York (1982).
10. C. Snyder, W. McIver and H. Sheffer. *J. appl. Polym. Sci.* **21**, 131 (1977).