

## Progress on polymerization of $\beta$ -pinene

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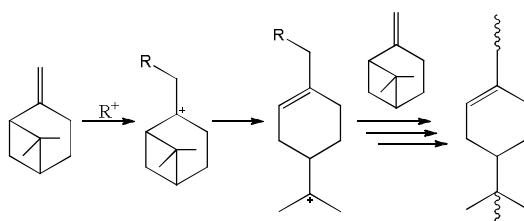
**Abstract.** Turpentine oil is one of the most important nature essential oil of the world and it is particularly rich in China.  $\beta$ -pinene is one of the principle components of turpentine oil. Turpentine has a high application value, but more applications are prepared terpene resin by polymerization. This paper reviewed the research progress on polymerization of  $\beta$ -pinene, including homopolymerization of  $\beta$ -pinene and copolymerization of  $\beta$ -pinene.

### Introduction

Turpentine is nature essential oil which is the largest production and cheapest in the world<sup>[1]</sup>.  $\beta$ -pinene is a naturally-occurring alicyclic monomer that is distillation product of turpentine. The most important commercial terpene resins are those resulting from  $\beta$ -pinene polymerization, although sometimes  $\alpha$ -pinene and dipentenebased resins can also be used<sup>[2]</sup>. Terpene resin which is from polymerization of  $\beta$ -pinene has a wide variety of industrial applications, such as adhesives and varnishes, additives in rubber, bituminous materials, food packaging and the production of chewing gums. Performance is determined by nature. This polymer has a outstanding properties: high solubility in hydrocarbon solvents, compatibility with waxes, relatively high softening point, nontoxic and inert to common chemicals<sup>[3]</sup>. The possibility of using to replace petrochemical raw materials has been attracting significant attention during the last decade. Due to the depletion of fossil oil reserves, terpene resins, which belong to renewable biomass resources, have been attracting significant attention as outstanding biomaterials during the last decade.

### Homopolymerization of $\beta$ -pinene

**Cationic polymerization.** In the beginning, the catalyst that is used in the synthesis of resin was the sulfuric acid. However, the catalytic performance of sulfuric acid is not good. From the beginning of the last century thirty's, lewis acid, such as aluminum chloride and its derivative, has becoming more and more common catalyst which is used for catalyzing polymerization of  $\beta$ -pinene. The Mechanism of the cationic polymerization of  $\beta$ -pinene is shown in Fig.1.



**Fig. 1** Mechanism of the cationic polymerization of  $\beta$ -pinene

The most common catalyst which be utilized to initiate polymerization of  $\beta$ -pinene is aluminum chloride which make cationic polymerization of  $\beta$ -pinene fast and thermally very violent. However, there are some limitations in using such a catalyst. Firstly, the catalyst needs to be used at low reaction temperature, which leads to high costs of production. In order to improve the reaction temperature, some researchers have made efforts. R. P. Guiné and J. A. Castro<sup>[2]</sup> use ethylaluminum dichloride ( $C_2H_5AlCl_2$ ) to catalyze the polymerization of  $\beta$ -pinene at relatively moderate temperatures. They studied the effects of temperature on the reaction and found that increasing temperature of polymerization make molecular weight and softening point decrease. Moreover, the color of resin become darker with increasing temperature. But they considered that high-quality resins can be produced at low temperatures that are industrially acceptable. Mohammad Hayatifar et al found that  $NbCl_5$  is highly effective for the polymerization of  $\beta$ -pinene at room temperature even this catalyst at low very concentration<sup>[3]</sup>.

Secondly, these catalysts (aluminum chloride and its derivatives) resulted in low molecular weight polymers. There are some ways to increase molecular weight polymers of poly( $\beta$ -pinene)s. N. A. Kukhta et al.<sup>[4]</sup> showed that  $AlCl_3$  etherates can efficiently prompt the polymerization of  $\beta$ -pinene at room temperature and low catalyst content (2.5–5.5 mM). The resultant of reaction (poly( $\beta$ -pinene)s) has relatively high molecular weight ( $M_n = 9\ 000 - 14\ 000\ g \cdot mol^{-1}$ ) and good thermal properties that include glass transition ( $T_g = 82 - 87^\circ C$ ) and degradation temperature. K. Satoh et al. reported that the polymerization of  $\beta$ -pinene is efficiently prompted by an initiating system, consisting of  $RCl$ ,  $EtAlCl_2$  and  $Et_2O$ , to afford relatively high molecular weight polymers ( $M_w > 100\ 000$ )<sup>[5]</sup>.

Thirdly,  $\beta$ -pinene polymerizes very fast and in a vigorous way after less than 1% of aluminum chloride is added. Y. Karasawa et al. have researched the controlled cationic polymerization of  $\beta$ -pinene. They found that a  $GaCl_3$ /alkylbenzene initiating system could be effective in inducing the controlled cationic polymerization of  $\beta$ -pinene, even be successfully produce well-defined polymers<sup>[6]</sup>.

In recent years, a variety of catalytics which are different from the lewis acid have been employed for the polymerization of  $\beta$ -pinene. The catalytic conversion of  $\beta$ -pinene to polymer was studied with silica-supported phosphotungstic acid. The result show that under the optimal condition, the polymer yield was up to 84.8 % and the number-average molecular weight was about 1 200<sup>[7-9]</sup>. Zengfang huang showed that in the presence of methylaluminoxane, 2-aminopyridine Ni(II) complexes could be highly efficient to catalyze  $\beta$ -pinene polymerization and afforded relatively high molecular weight polymers ( $M_w = 6\ 000 - 10\ 000$ )<sup>[10]</sup>.

### Copolymerization of $\beta$ -pinene

Copolymerizing  $\beta$ -pinene with other monomers could change the nature of the homopolymerization of  $\beta$ -pinene to produce copolymer with various properties, which expands the industrial application of  $\beta$ -pinene.

**Cationic polymerization.**  $\beta$ -pinene-Styrene resin is a kind of water-white or light colored resin with good thermal properties for practical use and a good solubility in aromatic compounds and aliphatic compounds. It is widely used in adhesive which require the light color and high thermal stability<sup>[11]</sup>. Using some catalysts, living cationic copolymerization of  $\beta$ -pinene and styrene was achieved. Phosphotungstic acid supported by activated carbon is such a catalyst. In the presence of phosphotungstic acid supported by activated carbon, the copolymer of  $\beta$ -pinene and styrene product yield obtained was 70.3% under suitable copolymerization condition. The average molecular weight of this copolymer up to 867 and it's distribution is 1.38<sup>[12]</sup>.

In addition to the direct polymerization of styrene and  $\beta$ -pinene with catalyst, Hui Liang et al. have studied the synthesis of  $\beta$ -pinene/styrene graft copolymer. Firstly, they utilized N-bromosuccinimide to brominate Poly( $\beta$ -pinene) on its allylic carbon. Then the brominated poly ( $\beta$ -pinene) was catalyzed by  $AlEt_2Cl$  to polymerize with styrene. In this way,  $\beta$ -pinene/styrene graft copolymer has been obtained<sup>[13]</sup>.

Other than styrene,  $\beta$ -pinene also can polymerize with other monomers by cationic polymerization. An-Long Li et al. deemed that  $\beta$ -pinene and isobutylene are similar in structure, which means that the

cationic random copolymerization of the two monomers is feasible. They utilized initiating system that consists of 1-phenylethyl chloride/TiCl<sub>4</sub>/Ti(OiPr)<sub>4</sub>/nBu<sub>4</sub>NCl to achieve the cationic random copolymerization of  $\beta$ -pinene and isobutylene in CH<sub>2</sub>Cl<sub>2</sub> at - 40 °C<sup>[14]</sup>. Using initiator to induce the copolymerization of different monomers, which is the traditional approach. However, Jiang Lu et al. give us a new idea in synthesis of poly( $\beta$ -pinene)-b-polytetrahydrofuran. Firstly, they synthesize macroinitiator which is poly( $\beta$ -pinene) carrying an active benzyl chloride terminal. Then using the macroinitiator to induce the ring-opening polymerization of THF with AgSbF<sub>6</sub> in the presence of propylene oxide at 20 °C, which obtain a new block copolymer of  $\beta$ -pinene and THF<sup>[15]</sup>.

**Radical copolymerization.** 2,2'-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) are traditional free radical initiators. jiesen Li utilized AIBN as initiator to induce the radical copolymerization of  $\beta$ -pinene and maleic anhydride in CH<sub>2</sub>Cl<sub>2</sub> at 90 °C. The results demonstrate that number-average relative molecular mass up to 14 000 and it's distribution is 1.59<sup>[16]</sup>. BPO also can be used to initiate the radical copolymerization of  $\beta$ -pinene and maleic anhydride in dioxane at 80 °C. The number-average relative molecular mass reaches as high as 18 500<sup>[17]</sup>. In addition, AIBN can induce the radical copolymerization of  $\beta$ -pinene and styrene<sup>[18]</sup>. BPO is also employed to initiate the radical copolymerization of  $\beta$ -pinene and 2,3,4,5,6-Pentafluorostyrene (PFS) at 70 °C<sup>[19]</sup>.

Except free radical initiators, Maria et al. have studied the effect of microwave on free radical polymerization. They found that the reaction time could be reduced under microwave irradiation<sup>[20]</sup>.

**Reversible Addition-Fragmentation Chain Transfer Polymerization(RAFT).** Living/controlled polymerization has become one of the hot research topics in the field of polymer synthesis chemistry, because it's an effective method to design and synthesize polymers accurately with mild conditions of polymerization. Reversible addition-fragmentation chain transfer (RAFT) polymerization is a kind of living/controlled polymerization. Compared with other living/controlled polymerization, RAFT is better at molecular design, because of its excellent applicability to monomers, along with mild reaction conditions. Many researchers have applied RAFT polymerization to the copolymerization of  $\beta$ -pinene and other monomer in recent years. Their research is shown in Table 1.

**Table 1.** Copolymerization of  $\beta$ -pinene and different Monomers in the Presence of Various RAFT Agents

monomer	$\frac{[M]_{total}}{[RAFT]/[AIBN]}$	RAFT Agent	Conversion (%)	$M_n$	$F_{\beta\text{-pinene}}$ (%)	Temperature (°C)	Time (h)
Acrylonitril <sup>[21]</sup>	950/4/1	CDB	24.5	4 840	17.6	70	72
		CED	39.0	8 200	17.5	70	72
		CPDB	26.0	4 750	17.8	70	72
Maleic Anhydride <sup>[22]</sup>	1000/3/1	PEPD	9.1	5 200	50.0	60	48
		PEDB	9.9	2 700	50.0	60	48
n-butyl acrylate <sup>[23]</sup>	875/2.5/1	CPDB	14	4 910	11.2	70	—
methyl acrylate <sup>[24,25]</sup>	1000/3/1	MEDB	8.2	9 680	5.6	70	22
		MEPD	27.4	12 920	5.7	70	22
		PEDB	7.5	5 010	—	60	8
POVB <sup>a[26]</sup>	666.7/2/1	PEPDA	13.9	9 900	—	60	8

<sup>a</sup> POVB is synthesized by  $\beta$ -pinene and 2- hydroxy -5- vinyl Salicylaldehyde

## Conclusion

$\beta$ -pinene, distillation product of natural turpentine, is a renewable natural resource. With the depletion of oil resources, applying  $\beta$ -pinene to polymer materials will be meaningful. However, the reaction temperature of  $\beta$ -pinene homopolymerization is still low, which leads to increase production costs and limits the commercial application of poly( $\beta$ -pinene)s. Copolymerization of pinene with other monomers only stay in theory research and can not carry out industrial production. Consequently, Studying on polymerization of pinene, especially its industrial application, is very important and has a bright future.

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