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POLYMERS FROM PINE GUM COMPONENTS: RADICAL AND COORDINATION HOMO AND COPOLYMERIZATION OF PINENES

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Abstract: The present work is aimed at studying the reactivity of α- and β-pinenes in radical polymerization. The pinene homopolymers obtained were oligomers, showing both isomers similar reactivities. In order to achieve products of higher molecular weight, the radical copolymerization of α- and β-pinene with methyl methacrylate and styrene was performed, giving rise to polymers with $\overline{M}_W$ varying from 11 500 to 53 000. In radical copolymerization α-pinene showed to be more reactive than β-pinene. All the radical reactions performed were carried out with a Ziegler-Natta catalyst, $TiCl_4/Et_3Al$, and with Et_3Al. Under the conditions tested, β-pinene did not undergo any polymerization reaction and the cocatalyst showed a pronounced catalytic effect. The coordination polymers obtained at 5 h had chain lenghts of the same order of magnitude of the corresponding radical copolymers obtained at 50 h, although for much lower overall conversion.

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INTRODUCTION

Pinenes (α- and β-pinene isomers, denoted α-Pin and β-Pin, respectively) are bicyclic natural monomers,and the main constituents of turpentine, which is obtained from the distillation of pine gum. Pinenes homopolymers belong to the family of terpenic resins that are low molecular weight hydrocarbon polymers, with values of $\overline{M}_W$ varying from 800 to 3000, prepared by cationic polymerization (Ref. 1). These are important commercial products used by the adhesive, sealant, wax coating and casting industries. A variety of modified polyterpene resins are obtained by cationic copolymerization with synthetic monomers and natural ones, like gum rosin. These are also low molecular weight products and find specific uses in the compounding of adhesives.

The cationic mechanism of pinenes polymerization is well known (Refs. 1-5) and due to his exocyclic double bond β-pinene shows higher reactivity than α-pinene.

In contrast to free radical systems, the reaction conditions (i.e. the nature of the solvent, and of the counter anion and the temperature) greatly affect the outcome of carbocationic copolymerizations. The effect of these reaction parameters and the kinetics are complex and interdependent (Ref. 6).

The aim of this work is to obtain pinene polymers with higher molecular weight than those produced cationically. To achieve this objective, bulk radical copolymerization was used and styrene (St) and methyl methacrylate (MMA) were chosen as comonomers, due to their higher reactivity. The radical homopolymerization of pinenes in the same conditions was also performed.

In the literature there is only one reference to pinene homopolymers via radical polymerization (Ref. 7). Very few studies were reported concerning radical copolymerization (Refs. 7, 8).

Some experiments were performed with a highly active Ziegler-Natta catalyst, $TiCl_4/Et_3Al$. The effect of the cocatalyst alone, both in the homo and copolymerizations was evaluated.

RESULTS AND DISCUSSION

In this study all the pinene homopolymers obtained were oligomers, under the form of yellow oils, in contrast to the copolymers, which most of them were white powders soluble in the unreacted mixture, with the exception of the copoly (α-Pin/MMA) which precipitated.

The conversion is defined, as $x_A=(M_{A0}-M_A)/M_{A0}$, for a monomer A, M_{A0} and M_A being the initial and the corresponding to a time t monomer concentrations, respectively. The evolution of the conversion with time of α- and β-pinene, during homopolymerization is shown in Fig. 1. The results of dM/dt were modelled by non linear regression analysis of the kinetic polymerization rate equation, being calculated the apparent kinetic constant $k' = k_p\,(f\,k_i\,/\,k_t)^{0.5}$. The k' values estimated were :

poly(α-pinene) $k' = 0.78\ \mathrm{mol}^{0.5}(\mathrm{cm}^3)^{0.5}\mathrm{h}^{-1}$ poly(β-pinene) $k' = 0.73\ \mathrm{mol}^{0.5}(\mathrm{cm}^3)^{0.5}\mathrm{h}^{-1}$

The evaluated parameters and the plots presented in Fig. 1, show that the pinenes radical reactivity is similar, in contrast to what is observed in the cationic reaction, when β-pinene is more reactive (Ref. 1).

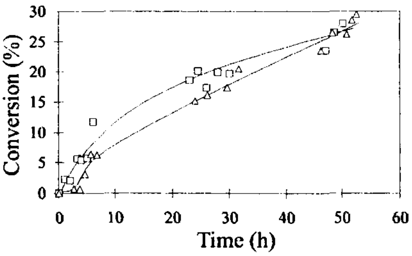


Fig. 1. Conversion versus time for α-pinene (□) and β-pinene (Δ) homopolymerizations. T=60°C, 2 (wt %) AIBN).

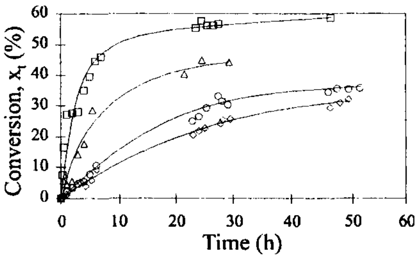


Fig. 2. Overall conversion versus time for the copolymerization systems α-Pin/MMA (□), β-Pin/MMA (Δ), α-Pin/St (o) and β-Pin/St (◊). Equimolar initial amounts of monomers, 2 (wt %) and T=60°C.

The reactivity of pinene isomers in the radical copolymerizations performed, was evaluated. The overall polymerization conversion is defined here as $x_t=(M_{10}+M_{20}-M_1-M_2)/(M_{10}+M_{20})$ (concerning comonomers 1 and 2). Fig. 2 presents the results of the conversion of both pinene (M_1) and synthetic monomer (M_2) versus time, in the copolymerization reactions performed. The analysis of the curves presented in Fig.2 show that the highest overall conversion was observed for the copolymerization system α-Pin/MMA, followed in a decreasing order by β-Pin/MMA, α-Pin/ST and β-Pin/St.

In Figs. 3A and 3B are plotted the individual conversions of each monomer, x_1 and x_2, along the reaction time, for all the copolymerization systems in study.

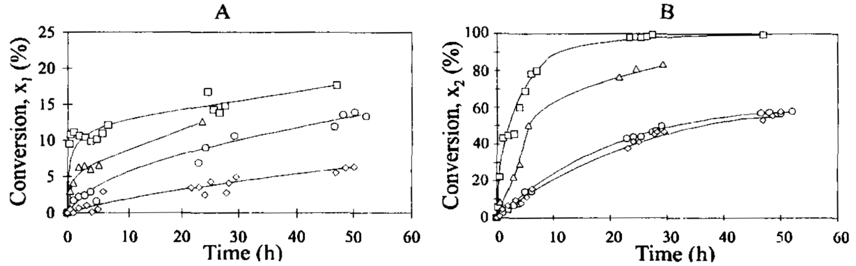


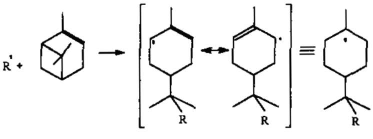
Fig.3. Conversions of terpenic and synthetic monomers versus time in copolymerization reactions (equimolar initial amounts of monomers, 2 (wt%) AIBN) and T=60°C).

Fig. 3A. α-Pin (□) in α-Pin /MMA
β-Pin (Δ) in β-Pin /MMA
α-Pin (o) in α-Pin/St
β-Pin (◊) in β-Pin/St

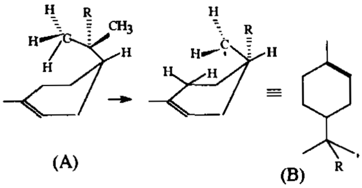
Fig. 3B. MMA (□) in α-Pin /MMA
MMA (Δ) in β-Pin/MMA
St (o) in α-Pin/St
St (◊) in β-Pin/St

In relation to each copolymerization system considered and based on Fig. 3A, it can be concluded that under the conditions tested α-pinene is more reactive than its isomer.

The similarity in the radical reactivity of the two pinenes isomers, can be explained by considering the pinene propagating radicals which can be formed in the initiation step. There are several hypotesis for the occurrence of different stable radicals, obtained from α- and β-pinene. For α-pinene five different radicals can be formed (radical species A to E), while for β-pinene only three hypothesis are suggested next (radicals F to H). This situation may explain the higher reactivity of α-pinene.

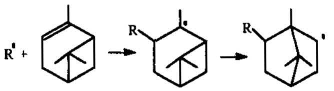


(A)

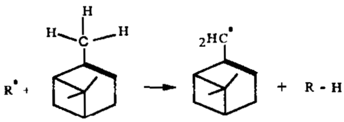


(A)

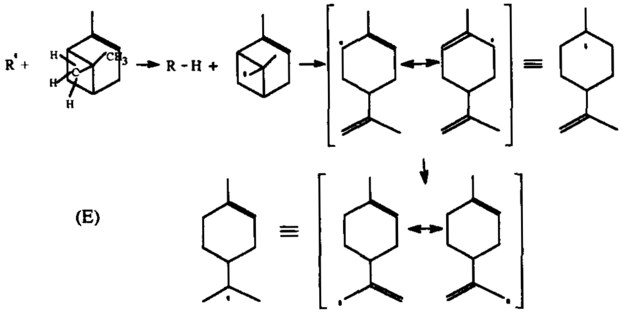
(B)



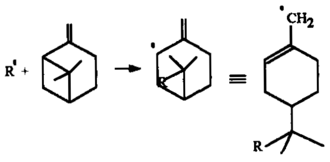
(C)



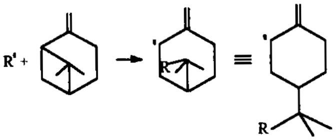
(D)



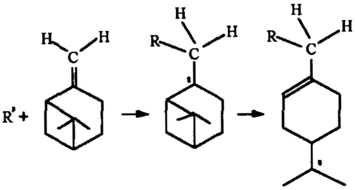
(E)



(F)



(G)



(H)

The overall conversion in radical and coordination homo and copolymerizations at the same reaction time (5 hours), is compared in Tab. 1. Using the Ziegler-Natta catalyst ($TiCl_4$/ Et_3Al) and the cocatalyst alone (Et_3Al), β-pinene did not undergo homo and copolymerization.

By comparison, the conversion values of radical polymers are higher than the corresponding to coordination polymers. Nevertheless, the chain lenghts of the α-pinene copolymers obtained with the $TiCl_4/Et_3Al$ catalyst at 5 h, have the same order of magnitude as the radical copolymers obtained at 50 h (Tab. 1). The cocatalyst alone has a pronounced catalytic effect, as can be concluded by the conversions obtained, which are only slightly inferior to the values obtained with the Ziegler-Natta catalyst, although the average molecular weights of the corresponding polymers are lower.

Tab. 1. Overall conversion (x_t,%) of all polymerizations after 5 hours of reaction. Weight average molecular weight ($\overline{M}_w$) and polydispersity ($\alpha = \overline{M}_w / \overline{M}_n$) of radical (AIBN 2% (wt.), T=60 °C, t=50 h) and coordination ($TiCl_4/Et_3Al$ and Et_3Al, 2% (wt.), T=80 °C, t=5h) polymers.

	AIBN			$TiCl_4/Et_3Al$			Et_3Al		
Polymer	x_t(%)	$\overline{M}_w$	α	x_t(%)	$\overline{M}_w$	α	x_t(%)	$\overline{M}_w$	α
Poly(α-Pin)	5.70	846	1.36	0.72	470	1.24	0.65	384	1.23
Poly(β-Pin)	4.80	882	1.40	–	–	–	–	–	–
Poly(α-Pin-co-MMA)	39.5	53152	1.97	6.05	61829	3.08	5.14	53152	1.97
Poly(β-Pin-co-MMA)	21.1	11584	1.52	–	–	–	–	–	–
Poly(α-Pin-co-St)	6.81	25806	1.91	1.37	20225	1.57	1.12	12862	1.54
Poly(β-Pin-co-St)	5.23	25388	1.73	0.65[a]	25672[a]	1.49[a]	–	–	–

[a] It was confirmed by infrared spectrometry and ^1H NMR that this polymer was styrene only.

It is reported in the literature the homopolymerization of α- and β-pinene with a titanium Ziegler-Natta catalyst ($TiCl_4$ based). The authors used as cocatalyst $Al(1\text{-}Bu)_3$ and $Al(i\text{-}Bu)_2Cl$, used various Al/Ti ratios (0.7-1), various temperatures (-80, 25 and 35 °C) and various reactions times (4 to 7 days) (Ref. 9). In the case of α–pinene the conversion did not exceed 2.3%, after 7 days of reaction time. Best results were obtained with the isomer β. A maximum conversion of 68% after 7 days was achived.

Tab. 2 shows the transition temperatures of the copolymers prepared by the two mechanisms.

Tab. 2. Transition temperatures, T_g and T_m, of radical (t=50 h, T=60°C) and coordination copolymers (t=5 h, T=80°C).

Polymer	AIBN		$TiCl_4/Et_3Al$		Et_3Al	
	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
Poly(α-Pin-co-MMA)	77	177	120	179	75	139
Poly(β-Pin-co-MMA)	64	133	-	-	-	-
Poly(α-Pin-co-St)	77	108	80	144	82	131
Poly(β-Pin-co-St)	59	97	-	-	-	-

EXPERIMENTAL PART

Bulk radical polymerizations were carried out at 60°C, for 50 h, in a 250 cm^3 stirred glass reactor, using 2% (weight on monomers) 2,2'-azobisisobutyronitrile as initiator. The binary copolymerization experiments were achieved with initial equimolar amounts of both monomers.

Coordination experiments were performed in n-hexane solution, in a 1000 cm^3 jacketed reactor BÜCHI-BEP 280, at 80°C, for 5 h. The titanium catalyst ([Ti] = 0.02 mmol dm^{-3}, Al/Ti = 100) and the cocatalyst were introduced under dried nitrogen. After closure the reactor was kept under 3 bar nitrogen presssure. The polymerization runs carried out with the Ziegler-Natta catalyst were repeated in the same conditions with the cocatalyst $AlEt_3$..

The composition of the residual monomer mixture was obtained by sequencial sampling, and the unreacted monomers were analysed by gas liquid chromatography (PYE UNICAM 4500 apparatus). The samples taken from the reaction systems α-pinene/styrene were analysed in a capillary column, type wall coated open tubular, with a silicone statonary phase, SE-30. In the analysis of the samples collected from the homopolymerizations and pinene/methylmethacrylate copolymerizations it was used a 20% Carbowax 20M (polyethylene glycol) column.

Average molecular weights were measured in a SEC equipment (WATERS), with a set of columns (Ultrastyragel) of 500 Å, 10^3 Å and 10^4 Å , at 30°C, using THF as eluent. The molecular weight determinations were obtained with a polystyrene standards calibration curve.

The transition temperatures were measured by differential scanning calorimetry at a heating rate of 5°C/min, in an equipment Setaram DSC92.

CONCLUSION

In radical homopolymerization the isomers α- and β-pinene showed similar reactivities, in contrast to their behaviour in cationic polymerization in which β- pinene is more reactive. The pinene homopolymers obtained were oligomers.

Under copolymerization conditions with the comonomers styrene and methyl methacrylate, α-pinene showed to be more reactive than its isomer β. The copolymers obtained were powders with $\overline{M}_W$ varying from 11 500 to 53 000.

All the radical reactions performed were carried out with a Ziegler-Natta catalyst, $TiCl_4/Et_3Al$, and with the cocatalyst alone. In the experiments carried out β-pinene did not undergo polymerization reaction. The cocatalyst showed a pronounced catalytic effect. The coordination polymers obtained at 5 h had chain lenghts of the same order of magnitude of the corresponding radical copolymers obtained at 50 h, even for much lower overall conversion.

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