

Polymerization of β -Pinene with Ethylaluminum Dichloride ($C_2H_5AlCl_2$)

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Received 22 July 1999; accepted 14 March 2001

ABSTRACT: The main goal of this work is to study the cationic polymerization of terpenes, particularly of β -pinene, with alkylaluminum catalysts. Some experiments at different polymerization temperatures (10, 20, and 50°C) were carried out with ethylaluminum dichloride catalyst, $C_2H_5AlCl_2$. From the results, it is possible to draw some general conclusions about the evolution of chain growth during polymerization. This work also includes the influence of reaction temperature on some properties of the final resin, particularly the molecular weight distribution, the softening point, and the Gardner color index. The role of reducing agents, such as iodine, during the distillation of the final resin is also evaluated with respect to color and softening point. As a result of this investigation, the Mark–Howink constants for terpene resins in toluene and dichloromethane as solvents have also been experimentally determined, thus allowing a more precise use of size exclusion chromatography in the characterization of such natural based products. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2558–2565, 2001

Key words: cationic polymerization; gel permeation chromatography; molar mass distribution; resins; terpenes

INTRODUCTION

Polyterpene resins are low molecular weight polymers obtained by cationic polymerization of certain terpenes. They are thermoplastics that can vary from viscous liquids to hard materials, and are stable to heat and ultraviolet (UV) radiation. Terpene resins combine with elastomers to give adhesives. However, it is not always easy to achieve the desirable values for some properties because these properties are strong functions of the average molecular weight of the polymer. As an example, ring and ball softening points between 115 and 135°C are required for most of their industrial applications. Moreover, because

they are stable, chemically inactive, nonirritating, and nontoxic, these resins are very often used in the food packaging industry.^{1,2}

The most important commercial terpene resins are those resulting from β -pinene polymerization, although sometimes α -pinene and dipentene-based resins can also be used. These resins can be prepared with different catalysts, the most common of which has been aluminum chloride. The limitations of such a catalyst, though, make its use prohibitive in the present situation. These limitations are associated with the requirements of low reaction temperatures and the high costs of cooling as well as with the high purity levels required for both reactants and solvents. Consequently, some studies have been carried out to investigate other types of catalysts, like alkylaluminum chlorides, which are almost insensitive to moisture.^{3,4}

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Journal of Applied Polymer Science, Vol. 82, 2558–2565 (2001)
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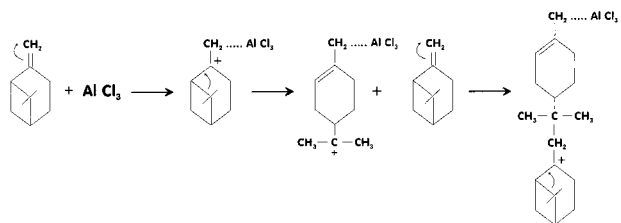


Figure 1 Mechanism for the polymerization of β -Pinene with aluminum chloride.

The cationic polymerization of β -pinene with strong Lewis acids is fast and thermally very violent, even with catalyst concentrations $< 1\%$. The reaction catalyst is a protonic complex, H^+G^- , which is formed by the interaction of a Lewis acid with the residual water present in the reaction mixture. It is important, therefore, to control the moisture content to avoid the deactivation of the catalyst by hydrolysis. The proton formed attacks the double bond of β -pinene, creating a carbenium ion whose structure is rearranged because of the transformation of a four-atom ring into a six-atom ring. The resulting species is much more stable and responsible for the attack on a new monomer molecule and therefore for propagating the reaction. The termination step occurs by rearrangement of the last unit, becoming a [2 : 2 : 1] bicycle system that, by loss of a proton, originates a camphenic group.^{1,2,5} The mechanism for the polymerization, as proposed by Roberts and Day⁵ for aluminum chloride, is illustrated in Figure 1.

When the polymerization occurs in the presence of an aromatic solvent, such as in solution polymerization, the phenomenon of transfer to the solvent is relatively important. It consists of the combination of the growing ion with the solvent molecules to form a neutral ending group by elimination of a proton. Depending on the desired molecular weight, the transfer to the solvent can become more or less important because it can eventually be a way of controlling the final molecular weight of the resin. The reaction ends by deactivation of the catalyst, with the addition of large quantities of water. The organic phase (polymer plus solvent) is then washed for removal of the catalyst and finally distilled for recovery of both the resin and the solvent.²

In a semidiscontinuous process, the monomer addition influences the molecular weight distribution because of the variation of the reaction medium properties; that is, viscosity, monomer concentration, and homogeneity.

The polymerization can be done by two different methods: direct and indirect. In the direct method, monomer is gradually added to a suspension of catalyst and solvent, whereas in the indirect method, the catalyst is added to a mixture of solvent and monomer. The former is most often used in the polymerization of β -pinene, of higher heat of reaction, because it enables a more efficient control of the heat generated in the reaction by varying the monomer flow.

POLYMERIZATION WITH ALKYLALUMINUM DICHLORIDE

Organometallic compounds, particularly di- or triorganoaluminum, have become increasingly important for the polymerization of olefins and diolefins because they lead to high molecular weight polymers at relatively high temperatures.³ Strong Friedel-Crafts acids, like AlCl_3 and EtAlCl_2 , produce spontaneous initiations in systems with reduced levels of moisture content because such low concentrations of water and other cationogenic impurities are sufficient to catalyze the initiation step. It is, however, necessary to assess their sensitivity to such impurities. For instance, in systems catalyzed by AlCl_3 , these impurities act as initiators only if their concentration is sufficiently low. In contrast to this, EtAlCl_2 -based catalysts are less sensitive to impurities, particularly water, and therefore are activated by such substances regardless of their quantity. This behavior enables a quick, efficient, and easy control of the initiation process. Weaker acids, like Et_2AlCl or Et_3Al , require the presence of a suitable cationogenic initiator, such as HCl or Cl_2 , to become as efficient as the stronger Lewis acids EtAlCl_2 and AlCl_3 in the presence of traces of water.^{3,4}

Although with AlCl_3 the range of favorable polymerization temperatures to produce long-chain resins varies from -50 to -10°C , with alkylaluminum dichloride this range is between -10 and $+30^\circ\text{C}$. This latter range corresponds to a much more attractive industrial situation because one can avoid the high operating costs associated with such low temperatures. There are, however, some disadvantages associated with the use of alkylaluminum chlorides. These compounds ignite spontaneously when in contact with air and may lead to violent reactions with water or strong oxidizing agents. Nevertheless, these properties are not a critical problem in industrial terms.^{3,6}

Table I Summary of Operating Conditions and of Main Results^a

Polymerization temperature (°C)	10		20		50	
Monomer quantity (g)	607.11		607.11		607.11	
% of α -pinene in monomer	1.2		1.1		1.1	
% of β -pinene in monomer	90.3		90.2		90.4	
Quantity of catalyst (g) [C ₂ H ₅ AlCl ₂]	≈ 20		≈ 20		≈ 21	
Quantity of solvent (mL) [toluene]	700		700		700	
Number of washings (resin)	4		4		4	
Number of filtrations (resin)	2		3		3	
Final mass obtained (g)	784		761		743	
Global yield (%)	65		51		44	
Resin code	R1a	R1b	R2a	R2b	R4a	R4b
Type of distillation (with steam and/or iodine)	Steam	Steam Iodine	Steam	Steam Iodine	Steam	Steam Iodine
Distillation temperature (°C)	200	200	200	200	200	200
Yield of distillation (%)	52	50	36	46	36	35
Gardner color	1 → 2	2 → 1	4	4	4	4
Ring and ball softening point (°C)	130.5	131	119	120	118	118.5
Average molecular weight \overline{M}_n	2432	1500	1128	997	882	880

^a Reference 7.

EXPERIMENTAL

Reactants

The preparation of the catalyst in the laboratory requires a careful procedure because of its dangerous properties and because of its crystalline state at temperatures < 30°C. The ethylaluminum dichloride was bought from Aldrich in sealed metal bottles containing 100 g of compound pressurized with nitrogen, that have to be kept in a glycerine bath at 60°C before the weighing process. This process is carried out with a heated syringe in a closed chamber of nitrogen atmosphere. Industrial grade monomer, containing ~ 90% of β -pinene, was analyzed by gas chromatography, filtered, and dried in a molecular sieve.

Chemical Reaction

All reaction experiments were carried out in a 3-L jacketed glass reactor connected to a cooling circulating bath for heat withdrawal. Approximately two hours after the cooling system is turned on, the reactor is filled with the solvent/catalyst mixture and the data acquisition system is activated. The valve of the nitrogen flow into the reactor is opened, and the reaction begins only when the valve controlling the monomer flow is opened. The monomer is added continuously with a controlled flow to maintain a constant temperature inside the reactor during the semi-discontinuous regime. During the reaction, 12–15 samples are col-

lected and poured into distilled water to immediately stop any further reaction. The resulting two-phase system is allowed to settle, and the resulting organic phase is then dried and analyzed by size exclusion chromatography (SEC).

After completing the addition of the desired quantity of monomer, which takes ~ 2 h, the reaction continues for 90 min more. When this time has expired, a significant amount of distilled water at room temperature is added with vigorous mixing to stop the reaction by deactivation of the catalyst. After ~ 30 min of interphase intimate contact, the two-phase reactor contents are transferred to decanting ampoules.

Extraction and Washing

After the mixture in the ampoules is perfectly separated into two different phases, the aqueous layer is rejected and the organic phase is washed with a solution of 0.6% HCl. For better contact, the content of the ampoules is vigorously stirred while washing and then left to decant once more. A few hours later, the solution of resin is further washed with a solution of 1% NaOH and 2% citric acid at 70°C. Finally, the organic phase is washed twice with water at 50°C and, after decanting, it is dried in a molecular sieve. All washing operations are carried out in a nitrogen atmosphere to avoid any contact of the resin with oxygen in the air.

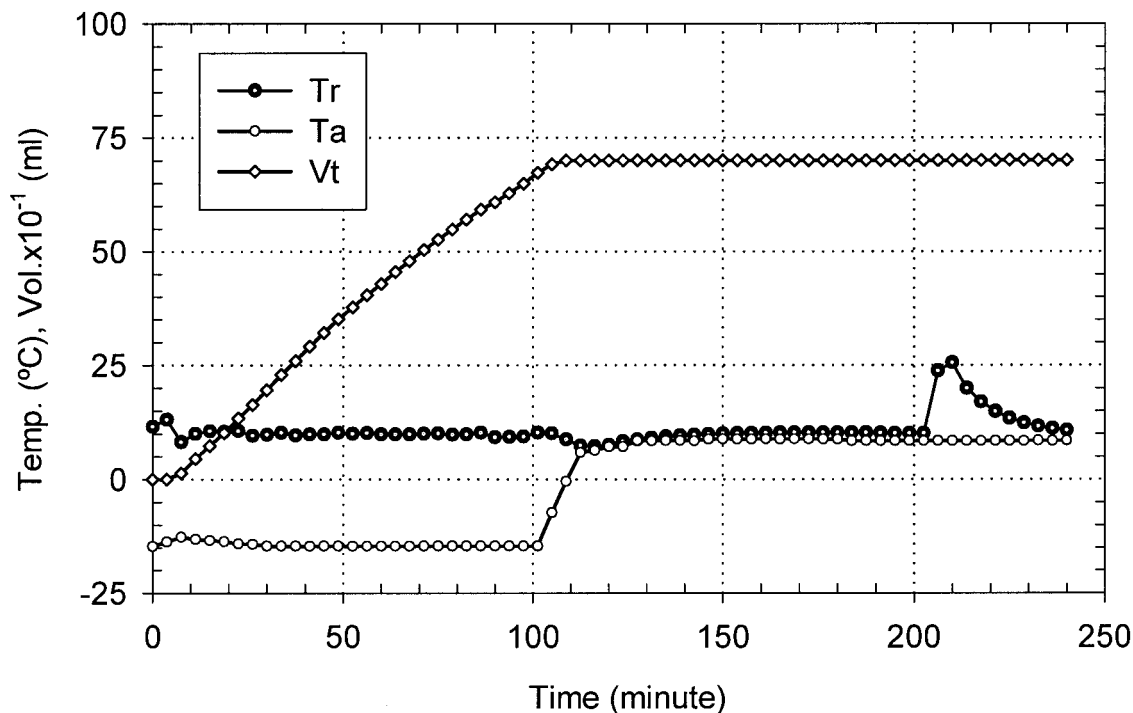


Figure 2 Profiles of total added volume of monomer (V_t) and reactor and jacket temperatures (T_r and T_a) during the polymerization run at 10°C .⁷

Distillation

Before distillation, the resin is filtered with diatomaceous earth as many times as necessary to obtain a transparent solution. Each filtration lasts 4–6 h and sometimes it is required to repeat the filtration up to four times. To accelerate the process, the filtration is done under vacuum in the presence of nitrogen. The final resin solution is then divided in two equal fractions that are distilled by the same process, but with and without iodine. During the distillation under a nitrogen atmosphere, the temperature is gradually increased up to 200°C . At $\sim 110^\circ\text{C}$, the solvent starts to vaporize and is collected after condensation with some traces of water. At this point, the temperature rise is slower, and between 140 and 180°C , steam is directly injected into the distillation flask. Globally, this phase lasts ~ 2 h.

To evaluate the role of iodine in minimizing the oxidation of the resin during distillation and thus, in preserving its color, iodine is first dissolved in 10 mL of toluene and added to the resin at the beginning of the operation. After distillation, the resin is cooled in small metal dishes at atmospheric conditions.

Analysis and Characterization of the Resin

The final resins and all the samples collected during the reaction period are analyzed by SEC (see Appendix), and the corresponding chromatograms transformed into molecular weight distribution curves. From these curves it is possible to monitor the time evolution of the molecular weight distribution and to determine the final average molecular weight.

The yields of the global process and of the distillation and filtration steps are also evaluated. Finally, the resin is characterized with respect to its ring and ball softening point and to Gardner color because these are the current industrial indicators of quality of the final product.

RESULTS AND DISCUSSION

In Table I, a summary of the operating conditions used in the laboratory trials and of the corresponding results is presented. In all experiments, the relative quantities of monomer, catalyst, and solvent were the same or approximate. The only operating variable that was varied from run to run was the temperature of polymerization.

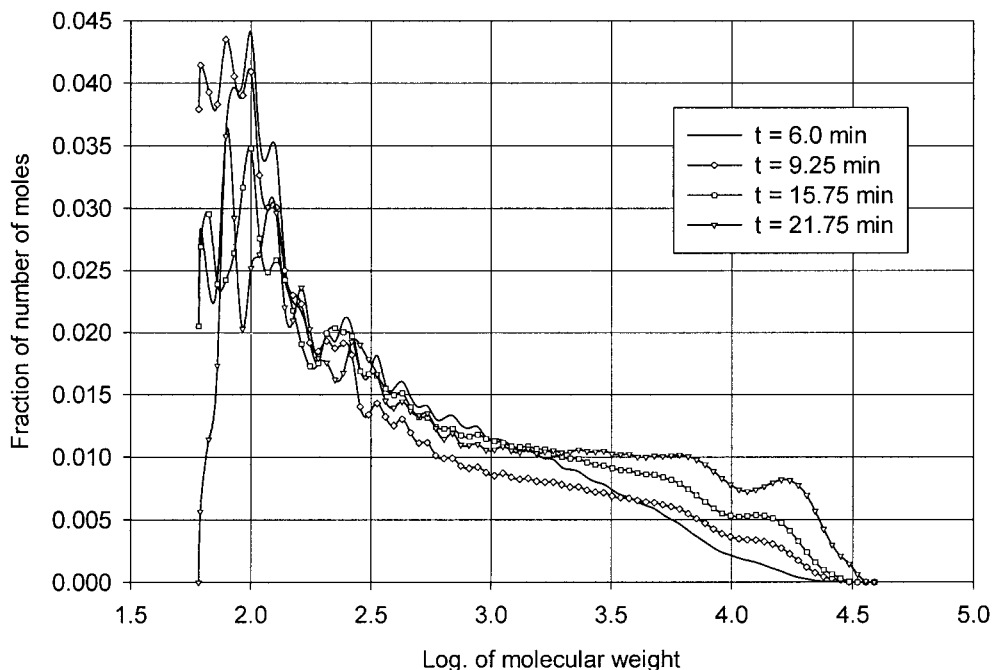


Figure 3 Evolution of numeric molecular weight distributions during the polymerization run at 10°C.⁷

The resins obtained at 10°C exhibit good properties, like high softening point and molecular weight, low color (showing some slight improvement in color when iodine was used in the distillation), and relatively high global yield.

The time evolution of the most important operating variables during the polymerization experiment at 10°C are illustrated in Figure 2. In the first 2 h, the temperature inside the reactor, T_r , was kept approximately constant and equal to 10°C using a temperature of -15°C in the cooling system. As can be seen, a driving force of ~ 25°C was imposed to remove all the heat generated by chemical reaction. During this period, the monomer was added gradually at an approximately constant rate until the total desired amount of the experiment, as shown in Curve Vt. When the addition of monomer comes to an end, the heat generated by reaction decreased enormously, and the cooling temperature had to be increased to ~ 10°C to compensate for this decrease. After 210 min, the reaction was terminated by addition of water at ambient temperature, creating a temporary increase in T_r , as can be seen in Figure 2.

The time evolution of the numeric molecular weight distribution of the resin during the polymerization experiment at 10°C is shown in Figure 3. After 6 min, the extension of the reaction is considerable but there is a special incidence of

dimers (at log molecular weight ≈ 2). As the reaction proceeds, the tendency for producing larger molecules is visible, and at 21.75 min, the presence of larger molecules accompanied by the peaks corresponding to molecules of two, three, four, and five monomer units is evident.

Considering the effect of temperature, there is a noticeable tendency for degradation in color with increasing values of temperature of reaction (Figure 4). This is also observed with regard to softening point and numeric average molecular weight (Figures 5 and 6). It is worth mentioning, however, that for the resin produced at 20°C, the

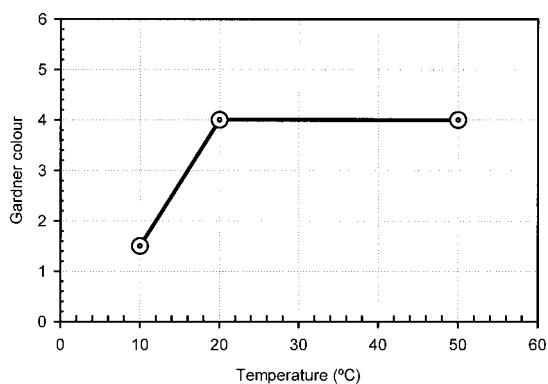


Figure 4 Influence of polymerization temperature in the Gardner colour of the resin.⁷

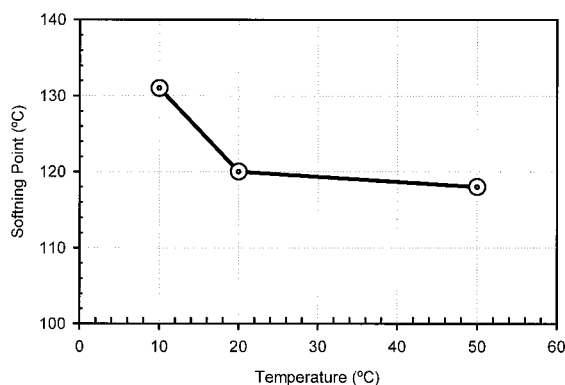


Figure 5 Variation of ball and ring softening point with reaction temperature.⁷

high values of the color indexes are due to an inefficient steam injection during distillation. This result confirms the extreme importance of the steam injection in producing clearer resins.

When the average molecular weight is plotted against the softening point for the resins distilled with and without iodine, a strong linear dependency is revealed, as shown by the straight lines in Figure 7, with correlation coefficients of 0.995 and 0.994, respectively.

CONCLUSIONS

From what has been discussed earlier, it is possible to draw the following general conclusions:

- Lower temperatures favor the global yield of the polymerization process.
- An increase in the temperature of polymerization gives rise to resins of lower molecular

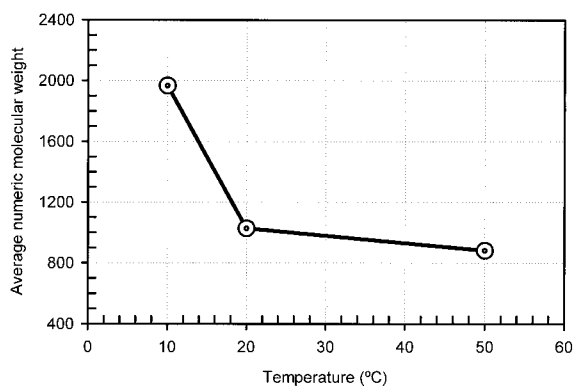


Figure 6 Variation of average numerical molecular weight with temperature.⁷

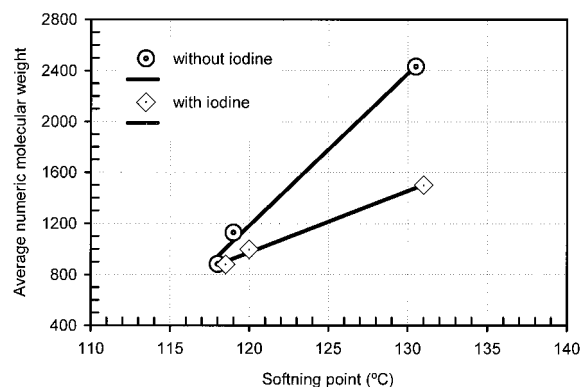


Figure 7 Variation of average numerical molecular weight with softening point.⁷

weight, lower softening point, and darker color. However, high-quality resins can be produced at low temperatures that are industrially acceptable.

- The use of iodine in the distillation does not show any significant improvement in the color of the resin. Further experiments revealed that a good steam injection plays a more important role for its clarification.

With the results achieved in this work, one can anticipate with some optimism the possible industrial application of this catalyst for the production of polyterpene resins and that such encouraging results can be achieved at relatively moderate temperatures.

Financial support from Luso-American Foundation (FLAD), Lisbon, is much appreciated. Special thanks are also due to NARES, Natural Resins, Ltd, St° Varão, Portugal, for providing all monomers used in the experiments and for carrying out all softening point and color index measurements.

APPENDIX

The molecular weight distributions were determined by SEC after the establishment of a cali-

Table AI Mark-Howink Constants at 25°C^a

Polymer	Solvent	K (mL/g)	a
Polyterpene resins	Toluene	0.0617	0.61
Polyterpene resins	Dichloromethane	0.1000	0.47
Polystyrene	Dichloromethane	0.1050	0.43

^a Reference 8.

Table AII First Part of Calibration Curve^a

Average Molecular Weight	Retention Time (min)
136.0	19.800
272.0	18.480
408.0	17.320

^a Reference 8.

bration curve for a system of columns for the particular case of the polyterpene resins. The chromatographic system consists of a high-pressure pump, a RI detector, and an injector, all from Perkin-Elmer. A set of three linear PLGel columns from Polymer Laboratories Ltd. was used.

The calibration curve was based on the use of isolated standards of monomer, dimer, and trimer, for the low molecular weight part. In addition to this, the Mark-Howink constants were determined for the high molecular weight region. These constants, K and a , are used in the following equation that relates the viscosity (η) with the average viscosity molecular weight (\overline{M}_v):

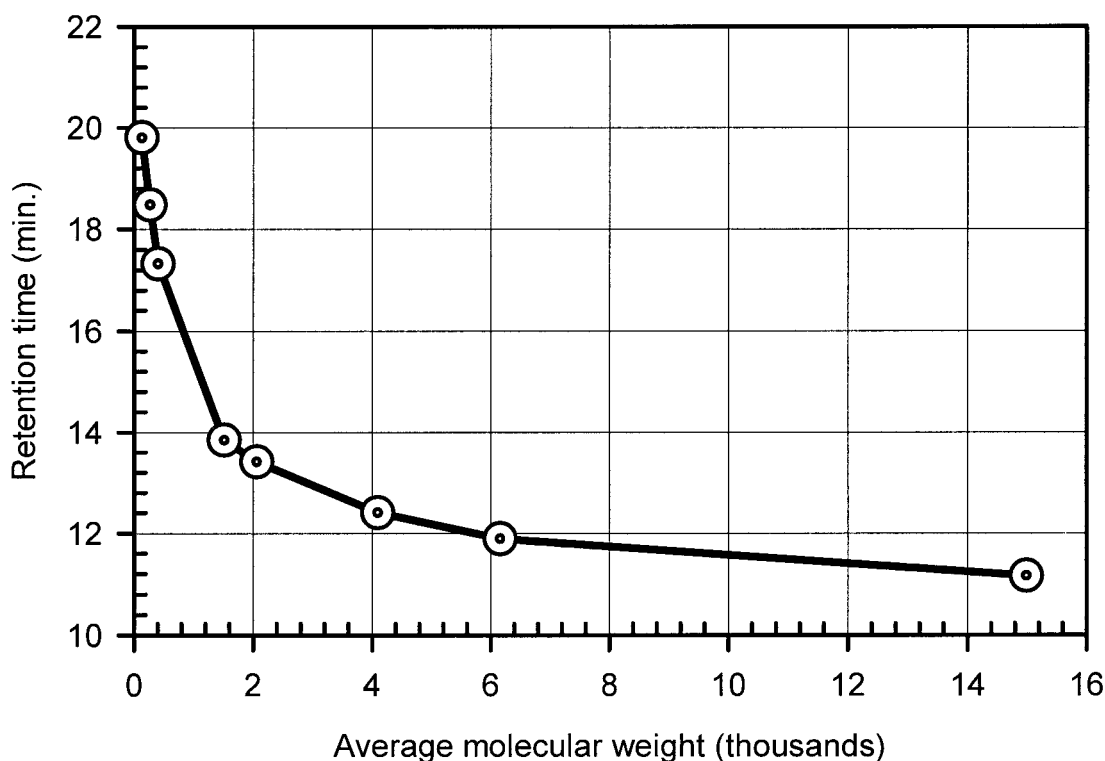
$$\eta = K(\overline{M}_v)^a \quad (\text{A1})$$

Table AIII Second Part of Calibration Curve^a

Average Molecular Weight	Modified Average Molecular Weight	Retention Time (min)
1800	1517.0	13.845
2470	2064.0	13.415
5000	4099.5	12.405
7600	6160.0	11.890
19,000	14,990.0	11.160

^a Reference 8.

Applying logarithms to eq. A1, K and a can be easily evaluated by plotting $\log(\eta)$ versus $\log(\overline{M}_v)$. For resins of low polydispersity, $\overline{M}_v = \overline{M}_w = \overline{M}_n$, and for this particular case, the absolute values of \overline{M}_n used in the evaluation of K and a were obtained by vapor pressure osmometry. On the other hand, the values of η were obtained by viscosimetry, using two solvents (toluene and dichloromethane) at 25°C. The values of the corresponding Mark-Howink constants are presented in Table AI.⁸

**Figure A1** Calibration curve for polyterpene resins.

The first part of the calibration curve was obtained directly from the knowledge of the retention times for the monomer, dimer, and trimer, determined experimentally and shown in Table AII. The second part of the curve was established with values of \overline{M}_w for polystyrene standards, modified by eq. A2 and using the Mark–Howink constants (see Table AIII). The resulting calibration curve for the polyterpene resins in dichloromethane with a flow of 1 mL/min is represented in Figure A1.⁸

$$\ln(M_s) = \frac{\ln\left(\frac{K_s}{K_t}\right) + (\alpha_s + 1)\ln(M_s)}{(\alpha_s + 1)} \quad (\text{A2})$$

where subscripts t and s stand for polyterpene resins and polystyrene, respectively.

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