

Effect of Aging Conditions of Neodymium-Based Catalysts on *cis*-1,4 Polymerization of Butadiene

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ABSTRACT: The aim of this work is to evaluate the effect of aging conditions catalysts based on neodymium salt on polymerization conversion, catalyst activity, and polymer characteristics. The synthesized catalysts were aged at 10, 25, 40, and 60°C for 24 and 48 h. The polybutadienes were characterized by size exclusion chromatography to determine the molecular weight characteristics and infrared spectroscopy to determine the microstructure. The results showed that the stereoselectivity of active catalyst sites was not affected by the aging condi-

tions. However, the molecular weight increased with aging temperature. The catalysts aged at 25°C showed a trend to attain higher activities than those aged at 40 and 60°C. Moreover, a significant drop on polymerization reaction rate occurred as the catalyst aging temperature increased. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1496–1502, 2009

Key words: Ziegler-Natta polymerization; neodymium; aging; catalysis; polybutadiene

INTRODUCTION

Lanthanide catalysts are efficient systems for dienes *cis*-1,4 polymerization. The catalysts stereospecificity depends on the metal used. When neodymium (Nd)-based catalysts are employed, higher *cis*-1,4 repeating units contents (98–99%) are attained. These catalysts have found applications in the field of elastomers for producing *cis*-1,4 polybutadiene.^{1–4}

To attain highly active catalyst systems, the Nd compound is combined with an alkylaluminum (AlR₃) and a halogen donor (halogenating agent). The most used Nd-based catalysts comprise Nd(III) carboxylates (also alkoxides or halides).^{5–9}

Two types of Nd systems can be used: binary systems derived from AlR₃ and a Nd complex of the type NdCl₃.*n*L where the ligand L may be tetrahydrofuran, alcohol, etc. The ternary system, in general, is constituted by a Nd(carboxylate)₃, an AlR₃, and an organic halide.

Ternary catalyst systems have been currently used in rubber industry to promote high *cis*-1,4 butadiene

polymerization (up to 98%). In this work, ternary system was used.

The chemical role of the different catalyst components and the nature of active catalyst species still are not well known. A change on catalyst synthesis parameters and polymerization conditions may affect the polybutadiene characteristics. The literature reports the existence of two different types of catalyst sites: a species which produces a polybutadiene with low molecular weight, that is supposedly deactivated during long periods of aging, and a second one responsible for producing polybutadiene with higher molecular weight, less sensitive to increasing of catalyst aging time.^{8–20}

The aim of this work was to evaluate the effect of catalyst aging conditions (time and temperature) on catalytic activity, polymerization conversion, polybutadiene microstructure, and molecular weight characteristics.

EXPERIMENTAL SECTION

Materials

The chemicals used in this work were diisobutylaluminum hydride (Akzo Nobel), neodymium versatate (Rhodia-Rare Earths and Gallium), *t*-butyl chloride (Aldrich Chemical Company), hexane (Petroflex S.A., Brazil), 3,5-*di-t*-butyl-4-hydroxytoluene (BHT) (Shell Brasil S/A, Brazil), trisnonylphenyl phosphite (TNPP) (GE Specialty Chemicals), butadiene (as hexane solution) (Petroflex S.A, Brazil), tetrahydrofuran,

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TABLE I
Influence of Aging Conditions on Polymer Microstructure

Aging conditions	Microstructure		Vinyl
	<i>cis</i> -1,4	<i>trans</i> -1,4	
10°C	98.2	1.2	0.6
24 h/25°C	98.0	1.4	0.6
48 h/25°C	98.0	1.4	0.6
24 h/40°C	98.2	1.2	0.6
48 h/40°C	98.1	1.4	0.5
24 h/60°C	98.0	1.3	0.7

PA (THF) (Vetec Química Fina, Brazil), and nitrogen (White Martins S/A, Brazil).

Catalyst synthesis

Catalysts were prepared in oven-dried nitrogen-purged bottles fitted with rubber septum. The order of components addition was diisobutylaluminum hydride (Al), neodymium versatate (Nd), and *t*-butyl chloride (Cl). The catalyst synthesis was carried out at 10°C, and the molar ratio of catalyst components was Al/Nd/Cl=11 : 1 : 3.²¹ Some catalysts were aged at 10, 25, 40, and 60°C for 24 h, and the others were aged at 25 and 40°C for 48 h.

Polymerization

All polymerizations were carried out in a 1 L stainless steel Parr reactor. The reaction system was inertized through purge with extra dry nitrogen, additionally treated in drying columns packed with activated alumina. To the Parr reactor was added a dry hexane solution of butadiene (35% wt/wt) followed by the addition of dry hexane. The reaction medium was heated up to the stated reaction temperature and then the catalyst was injected (by syringe). The polymerization temperature employed was 70°C. Polymerizations were terminated after 2 h by adding a hexane solution of BHT (50% wt/wt) and stabilized by adding a hexane solution of TNPP (10% wt/wt). The polymer was coagulated under stirring in distilled water at 75°C for 1 h. Finally, it was dried in an oven at 60°C until constant weight. Polymerization conversion was calculated relating the polymer mass obtained to the monomer mass fed to the polymerization reactor.

Polymer characterization

Polymer microstructure was characterized by infrared spectroscopy in Perkin-Elmer equipment, model Spectrum One, as films formed on KBr cells, prepared from 2% (wt/v) chloroform solutions. The iso-

mer repeating units contents were obtained from the absorbances at 725 (*cis*-1,4), 910 (1,2-vinyl), and 965 cm^{-1} (*trans*-1,4). Polymer molecular weight characteristics were evaluated by size exclusion chromatography (SEC), in a Waters 150-C Plus SEC, fitted with a RI detector at 30°C, using THF as solvent at 1 mL/min flow rate. It was used a universal calibration curve, constructed by using polystyrene monodisperse standards. Polymer solutions (0.1% wt/wt) were filtered through filters of 0.45 μm pore diameter before injecting in the SEC equipment.

RESULTS AND DISCUSSION

The microstructure of polybutadiene practically was not affected by the variation of the catalysts aging temperature (Table I). The *cis*-1,4 units content remained between 98.0 and 98.2%, and the *trans*-1,4 units between 1.2 and 1.4%, and the vinyl units

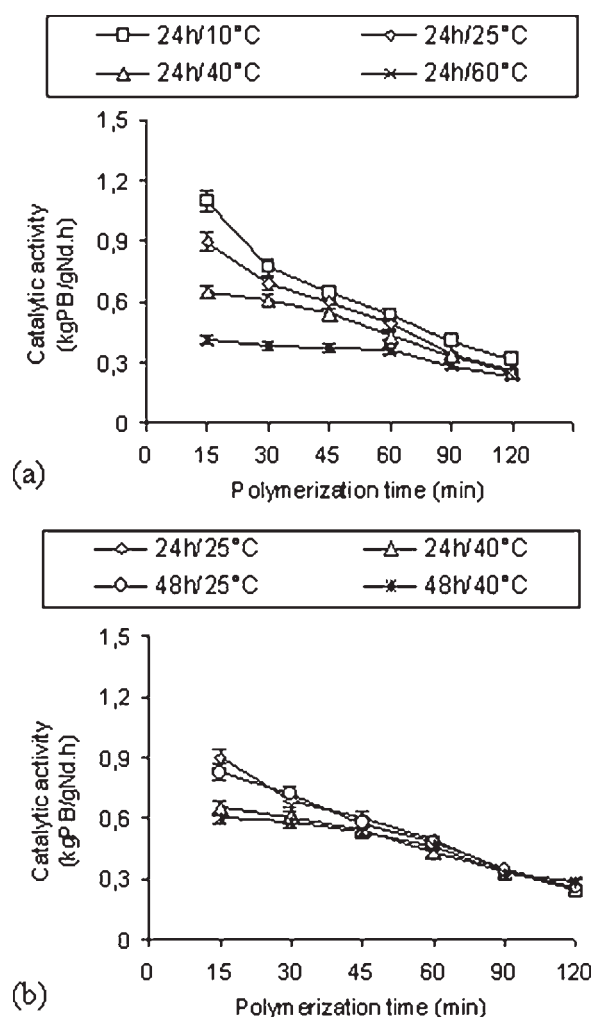


Figure 1 Influence of aging conditions on catalytic activity (PB, polybutadiene).

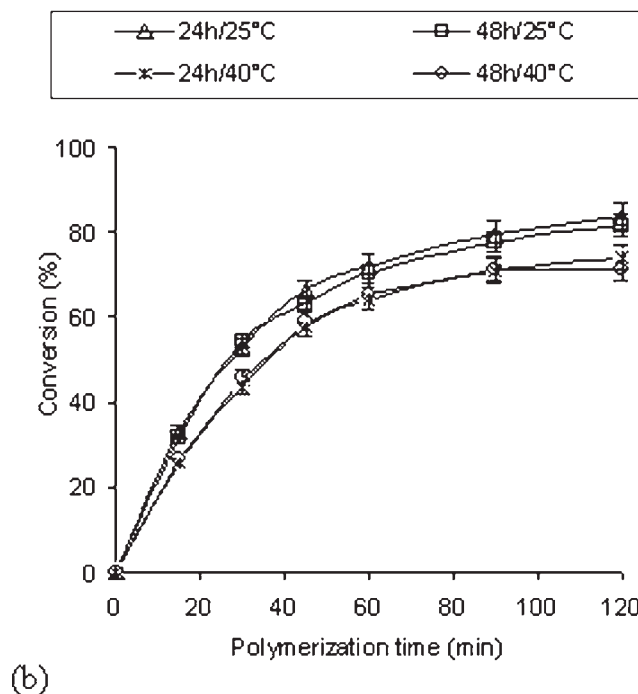
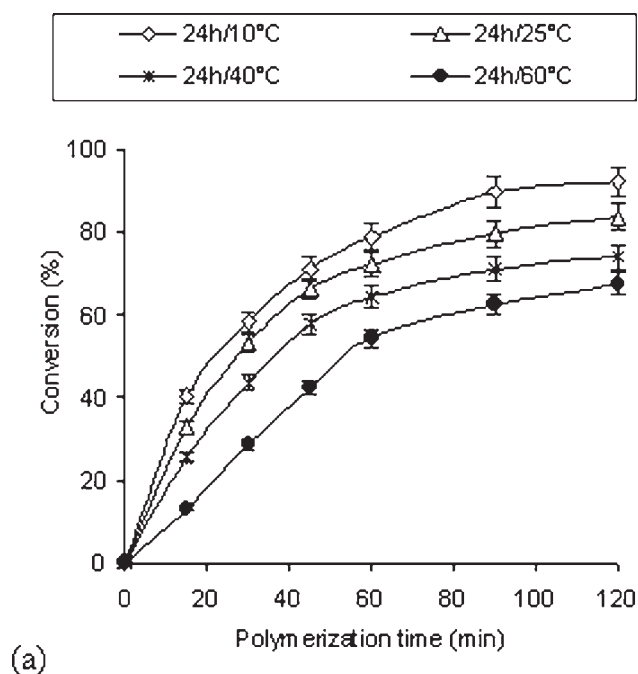


Figure 2 Influence of aging conditions on the polymerization conversion.

between 0.5 and 0.7%. Thus, one can conclude that stereoselectivity of the active sites was not affected by the aging conditions tested in this work.

Figure 1 shows that an increase on the catalyst aging temperature to 60°C tends to decrease the initial catalyst activity. The catalysts aged at 25°C showed a tendency to attain higher activities than those aged at 40 or 60°C for the same period of time.

That behavior was confirmed by the lower conversions obtained by the catalysts aged at 60°C [Fig. 2(a)].

In a general way, an increase in the temperature favors the occurrence of a chemical reaction. However, Pires²¹ verified that the alkylation step of Nd is not a reaction favored by the temperature. This behavior can be attributed to the fact that σ Nd–C bonds, formed in the alkylation stage, are more stable at lower temperatures.²² Thus, the lower activity at higher temperatures may be a consequence of thermal degradation of these catalytic species.

The decrease of the propagation rate constant (k) as the polymerization time increased (Fig. 3) may be attributed to some factors, such as deactivation of active sites, and the medium viscosity increase (as the polymerization progresses) making difficult the monomer diffusion through the reaction medium.

According to Friebe et al.,²⁰ the polymerization rate is given by eq. (1). Considering the initial monomer concentration $[M_0]$ and the neodymium

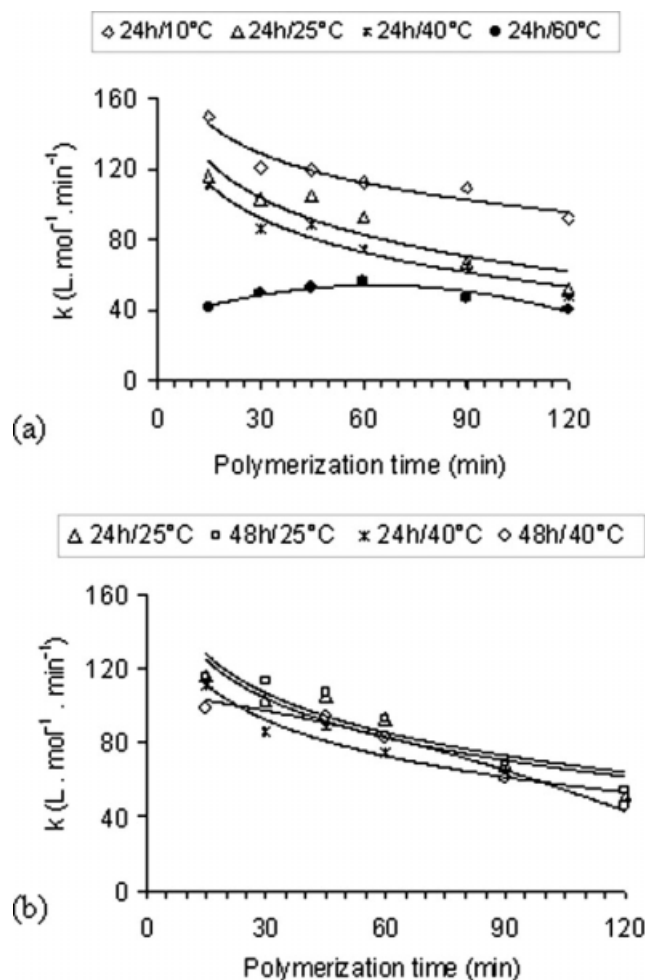


Figure 3 Influence of aging conditions on propagation rate constant.

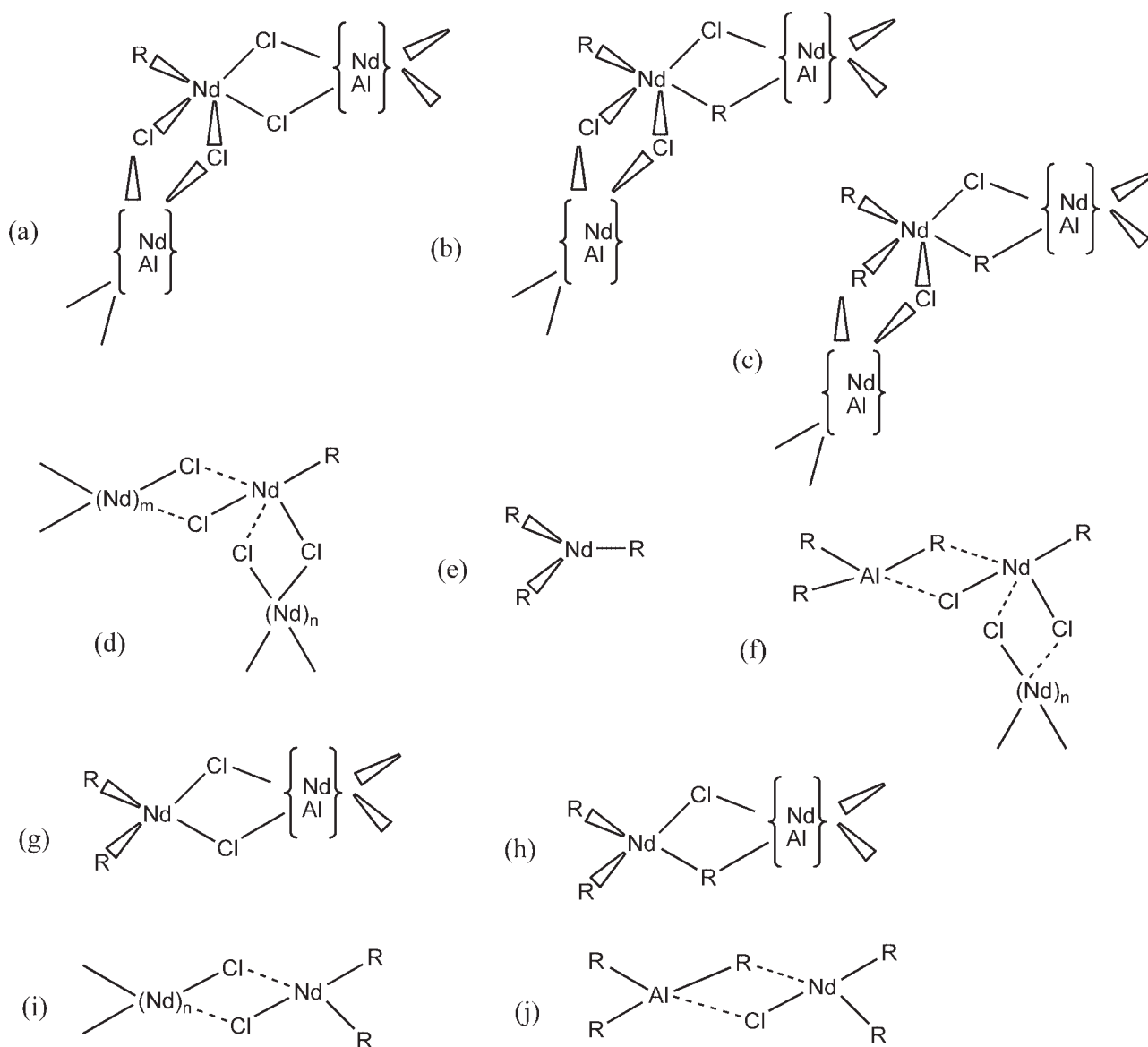


Figure 4 Possible structures of catalytic sites.

concentration $[Nd]$ constant, it is possible to obtain the propagation rate constant (k) [eqs. (2) and (3)].

$$\frac{\partial[M]}{\partial t} = k[Nd][M] = k^*[M] \quad (1)$$

$$k^* = \frac{-\ln([M]_t/[M]_0)}{t} = \frac{-\ln(1-x)}{t} \quad (2)$$

$$k = \frac{k^*}{[Nd]} \quad (3)$$

where $[M]_t$ is the monomer concentration at the reaction time " t ," " x " is the conversion degree, $[Nd]$ is the concentration of all Nd species, and " t " is the polymerization time.

It is possible to observe a decrease on the reaction rate as the catalyst aging temperature increased [Fig. 3(a)]. Probably that occurred because some active sites were progressively deactivated at higher temperatures.

The polymerization conversion [Fig. 2(b)] and propagation rate constant [Fig. 3(b)], practically, were not affected by the increase of aging time from 24 to 48 h. These results suggest that the number of active sites formed in both catalyst systems was very close.

In accordance with literature,²³⁻²⁷ there are several active sites with different sensibilities in relation to aging. The structure of the catalytic sites is one of the main factors affecting all parameters of a catalytic system. Some possible structures for these sites

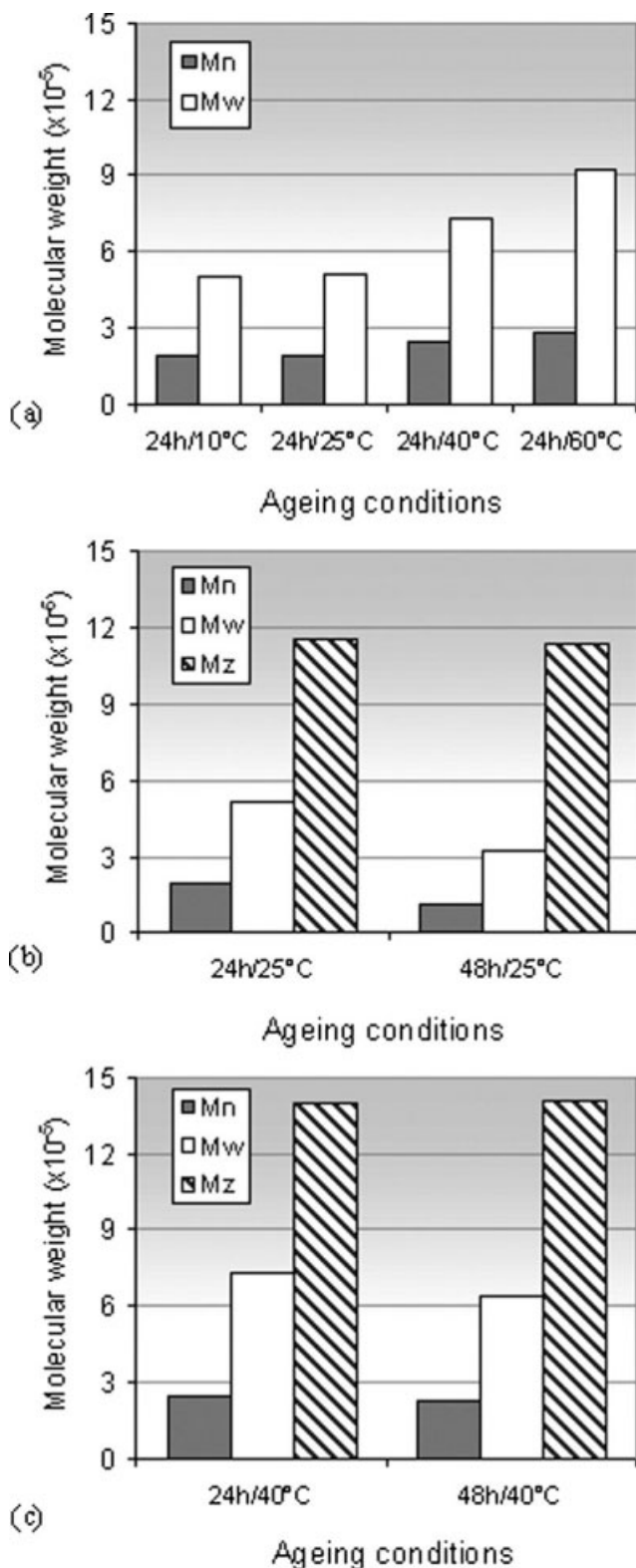


Figure 5 Influence of aging conditions on polybutadiene number-average molecular weight (Mn), weight-average molecular weight (Mw), and z-average molecular weight (Mz).

are shown in Figure 4.^{23–27} Most of them are bimetallic complexes and involve an alkylated lanthanide metal. In addition, they differ both in the environ-

ment of the lanthanide atom (number of Cl and C atoms) and in the number of lanthanide–carbon bonds at which the polymer chain propagates. The existence of these different types of active sites does not mean that they all are present at the same time. In each particular catalytic system, different types of active sites can be formed and the proportion of each one of them depends on the preparation conditions employed. Thus, the increase of the aging temperature may have provoked the deactivation of some active sites and, consequently, the reduction of the reaction rate. Hence, in this study, probably the predominant catalytic species during the polymerization reaction are the bimetallic ones that contain a lower number of σ Nd–C bonds because these bonds are more unstable at higher temperatures.²²

The possibility of occurring deactivation of active sites can be confirmed by the results of molecular weight determinations (Fig. 5). The molecular weight showed a tendency to increase as the aging temperature increased. Hence, if the conversion diminished

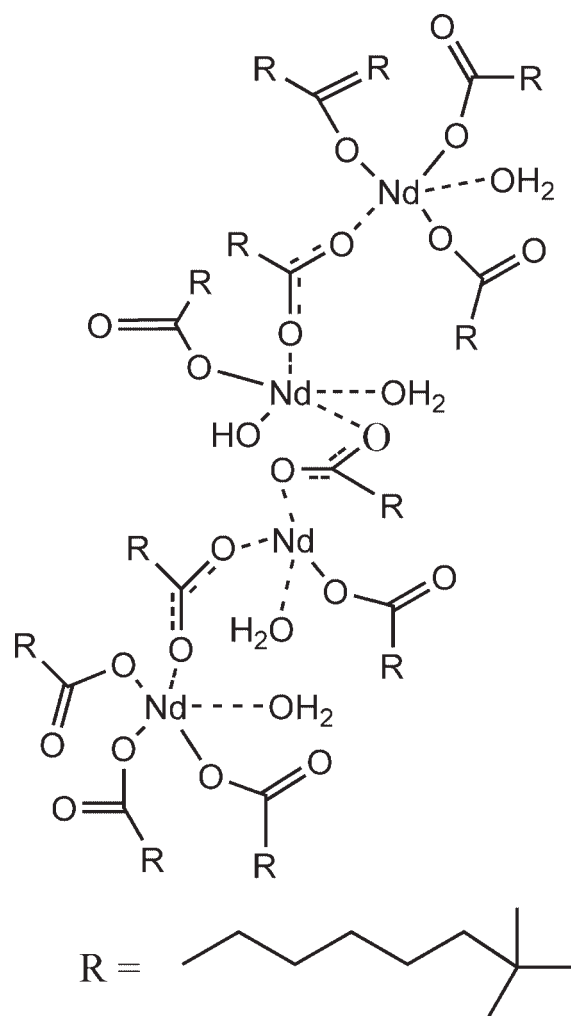


Figure 6 Neodymium versatate structure.

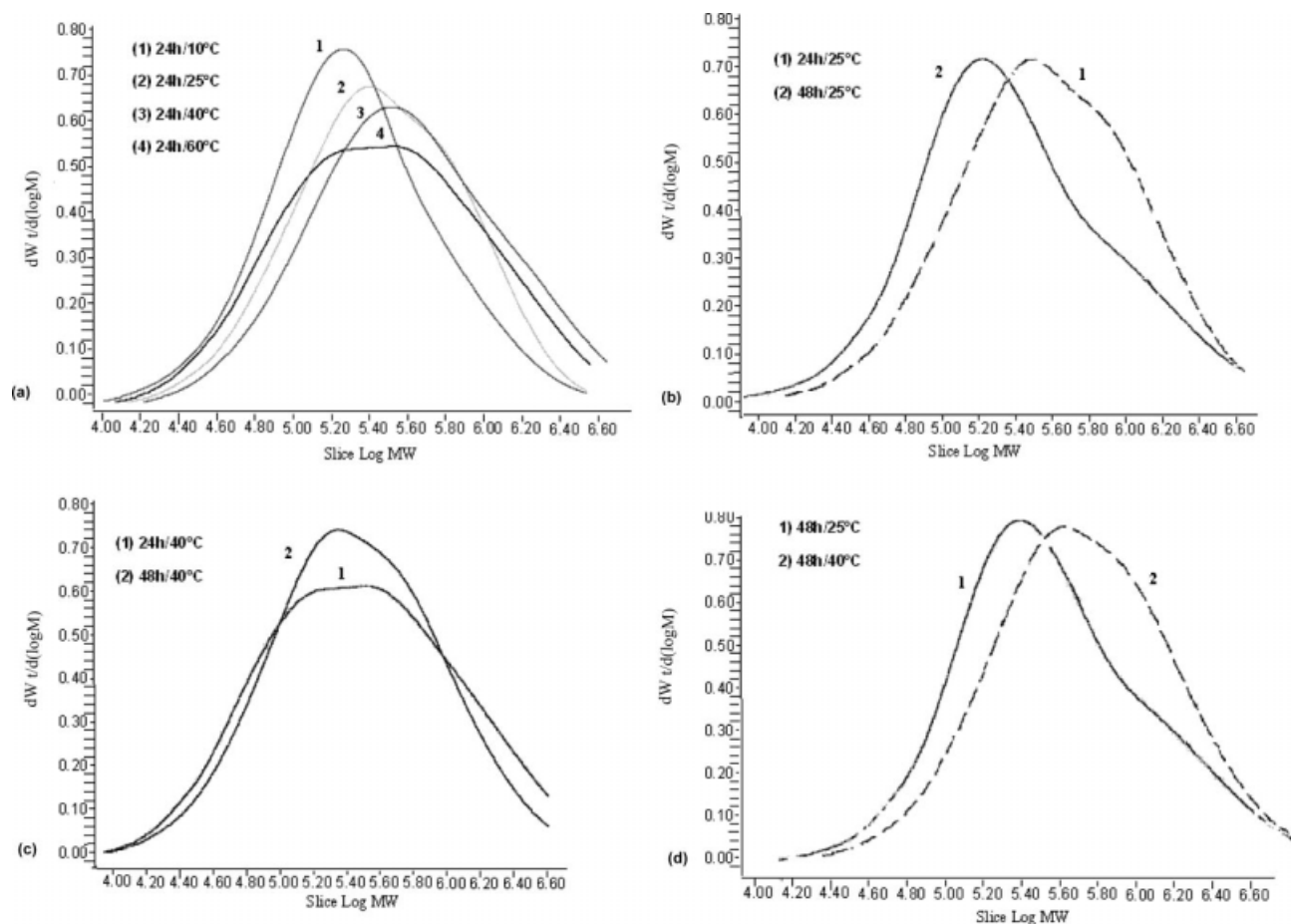


Figure 7 Molecular weight distribution curves of polybutadiene.

and the molecular weight increased, probably, a reduction on the number of active sites occurred, this behavior is in accordance with Wilson and Jenkins.²⁸

The tendency to molecular weight increasing, at higher temperatures, can be also explained by the presence of thermally stable catalytic species, which are less active.

Kwag et al.^{22,29} verified that neodymium versatate molecules are associated, forming oligomeric or polymeric structures, with polar ligands, such as water, hydroxide, and carboxylates, which saturate the coordination sphere of Nd (Fig. 6). Thus, the Nd atoms located in the most external zone of that structure would be more easily alkylated and after that chlorinated (because they are more exposed) forming the active sites. These sites are more unstable, because they are more susceptible to deactivation than the sites located in the most internal zone of the neodymium versatate structure. Thus, it can be considered that the more unstable active sites would be the responsible ones for producing the polymer fraction with lower molecular weight. This can explain the trend of molecular weight increasing

verified in this work. Thus, the predominant active sites after the catalyst aging are the responsible ones for the formation of polymer fractions with higher molecular weight.

Figure 7(a) compares the profile of molecular weight distribution (MWD) curves of polybutadienes produced with catalysts aged in different temperatures. It can be observed that it has a trend to obtain bimodal MWD curves for polymers produced by catalysts aged for 24 h at 25, 40, and 60°C. Moreover, it had a displacement of the curves for the region of higher molecular weight as the aging temperature increased, thus confirming the active sites that had remained active after the aging could be the responsible ones for the polymer fractions with higher molecular weight.

The difference found in the values of molecular weight is significant for Mn and Mw, whereas the z-average molecular weight (Mz) (more sensible to the fractions of higher molecular weight) practically did not vary [Fig. 5(a,b)]. Probably, the sites that remained active after the aging period are responsible for polymer fractions with lower molecular weight, which may explain the reduction of

molecular weight observed in this work. This fact was proven by comparison of MWD curves profiles obtained by SEC [Fig. 7(b)]. It can be observed a displacement for the region of lower molecular weight for the polymers whose catalysts had been aged by 48 h at 25°C.

Figure 7(d) shows that the increase of aging temperature provoked a displacement of the curve for the region of higher molecular weight. Thus, the active sites that had remained active can be responsible for the polymer fractions with higher molecular weight. This also contributes for the increase of molecular weight verified in this work. This is confirmed by Oehme et al.,²³ which concluded in their work, that for these catalytic systems, the existence of active sites responsible for producing polymer fractions with high molecular weight that would be resistant the higher temperatures of aging.

CONCLUSIONS

The microstructure of polybutadiene practically was not affected by the variation of catalysts aging conditions. A significant decrease on the reaction rate as the catalyst aging temperature increased has occurred. The molecular weight showed a tendency to increase as the aging temperature increased. Probably that was so because the sites that remained active after the catalyst aging are the responsible ones for the formation of polymers with the highest molecular weight. The polymerization conversion and propagation rate constant, practically, were not affected by the increase of aging time from 24 to 48 h. However, the molecular weight presented a trend to diminish as the aging time increased.

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