



# The thermo-oxidation of isoprene containing copolymers of isobutylene: Activation energies and reactions from room temperature to 100 °C



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## ABSTRACT

The activation energies of two poly(isobutylene-co-isoprene) (IIR) copolymers containing 0.9 and 1.85 mol% isoprene were determined under thermo-oxidation conditions from ambient to 100 °C. Transmission Fourier Transform Infrared (FTIR) spectroscopy was used to follow the functional group development. Ketone generation was the dominant oxidative product above 70 °C whereas below this temperature, carboxylic acid formation was prevalent. Non-Arrhenius kinetic behavior was observed due to curvature taking place near 70 °C. The estimated activation energies for the high and low temperature degradation processes were 85–87 kJ/mol and 49 kJ/mol. Test results were interpreted in terms of two competing thermo-oxidative zones, isobutylene and isoprene, the latter operating at low temperatures as shown by isoprene depletion and chain scission reactions. A set of thermo-oxidative reactions for IIR copolymers is proposed comprising allylic and addition reactions at the isoprene unit.

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## 1. Introduction

Accelerated heat aging in the 40–100 °C range and functional group analysis by transmission FTIR spectroscopy have recently been applied to investigate the thermo-oxidation of poly(isobutylene) (PIB) [1]. Oxidation product evolution was continuous within the tested temperature range and displayed linear Arrhenius behavior which allowed for an Activation Energy ( $E_a$ ) range of 116–125 kJ/mol for the growths of the carbonyl (ketone), hydroxyl and  $\beta$ -lactone groups. The evolution of PIB thermo-oxidative products is well understood [2,3].

Poly(isobutylene-co-isoprene) or butyl rubber contains 0.7–2.2 mol% of isoprene for the main purpose of crosslinking. The polymerization process inserts the isoprene units randomly in the prominent head-to-tail 1,4 configuration [4] and although normally reported as linear in nature, some branching occurs due to a rearrangement reaction [5]. Lifetime prediction of butyl based articles is of interest in order to assess durability in terms of both shelf and service lives upon exposure to conditions where thermo-oxidative processes are taking place. The thermal degradation of IIR has been

investigated at high temperatures by using techniques such as thermogravimetric analysis (TGA) and calorimetry [6–10].  $E_a$  values for 0.6–2.0 mol% IIR by TGA were essentially identical (124–125 kJ/mol) [6]. Increasing the isoprene concentration to the range of 2–2.5 mol% caused the value to decrease to 105–108 kJ/mol. By using IR spectroscopy in the 160–205 °C range,  $E_a$  values of 106 and 97 kJ/mol were calculated for 1.6 and 2 mol% IIR [11]. The research group at Sandia Laboratories has been quite active investigating lifetime behavior of formulated butyl compounds [12–14]. Compressive stress relaxation (CSR), density, elongation to break and oxygen consumption yielded  $E_a$  values of 80–86 kJ/mol for accelerated aging in the 50–125 °C temperature range [12]. No curvature in the data set was observed when the 25 °C oxygen consumption shift factor was included. Subsequent life time work on a peroxide cured butyl compound (Butyl-B) by oxygen consumption displayed curvature in the Arrhenius plot around 80 °C with high and low temperature deduced activation energies of 101.5 and 75 kJ/mol respectively [13]. Most recently, the compression set aging data from 60 to 100 °C for butyl compounds were best described by using two activation energies (127 and 59 kJ/mol) due to curvature in the data around 75 °C [15]. Non-Arrhenius behavior due to two competing reaction processes at high and low temperatures is prevalent in other polymer systems [16]. In

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summary, a wide range of activation energies (59–125 kJ/mol) have been observed for butyl rubber in the literature, warranting further investigation.

The thermo-oxidative reactions responsible for the chain scission in IIR copolymers are less understood. Early work on the thermal degradation of IIR by TGA and calorimetry emphasized the preponderance of chain cleavage reactions in the isobutylene containing zones with thermo-oxidation proceeding through hydroperoxide formation [6]. Jipa et al. have put forth reaction mechanisms through attack on the allylic group of the isoprene unit going through hydroperoxide formation and decomposition, followed by chain scission reactions leading to an array of oxidative products (ketones, aldehydes, acids) [11]. Their conclusions however, come from results obtained through high temperature thermo-oxidation (160–205 °C) conditions which likely neglect reactions taking place in the low temperature regime.

In order to better estimate the activation energy and to comprehend the underlying reaction mechanisms taking place during thermo-oxidation, unfilled and unstabilized IIRs will be studied. The low temperature regime will be in particular investigated by heat aging samples from 40 to 100 °C. Ambient aged samples will also be included. Transmission FTIR spectroscopy will be used to follow functional group development in the carbonyl zone. Shift factors from Time Temperature Superposition (TTS) will be used to calculate activation energies assuming Arrhenius kinetic behavior of the thermo-oxidative degradation processes. Finally, through the observation of the product evolution by FTIR and NMR, a set of thermo-oxidation reactions for IIR copolymers will be proposed.

## 2. Experimental

Both poly(isobutylene-co-isoprene) copolymers were kindly provided by LANXESS Inc. (RB100, 0.9 mol% isoprene; Butyl 301, 1.85 mol% isoprene). These will be identified by 0.9IIR and 1.85IIR respectively. The sample preparation procedure and the FTIR method for data collection and spectra normalization are summarized in Ref. [1].

Air circulating ovens (Binder) set at 40, 50, 60, 70, 80, 90 and 100 °C were used for heat aging. A set of samples was also kept in the dark in a fumehood and allowed to age at ambient temperature.

Fourier transform <sup>1</sup>H Nuclear Magnetic Resonance (NMR) was carried out on unaged and selected aged samples using a 400 MHz Bruker BioSpin system. Samples were dissolved in deuterated chloroform and tested at 25 °C. 256 scans were employed with a relaxation delay of 1 s. TopSpin 3.1 software was used for data acquisition and subsequent processing.

After application of the TTS procedure for a given reference temperature  $T_{ref}$ , the calculated shift factors  $a_T$  were used in order to estimate an activation energy  $E_a$  for the thermo-oxidative processes assuming steady-state Arrhenius degradation (eq. (1)).

$$a_T = \exp \left[ \frac{E_a}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (1)$$

R represents the ideal gas constant (8.314 J/K/mol).

## 3. Results and discussion

### 3.1. Oxidative products by FTIR

The evolution of the FTIR bands in the hydroxyl, carbonyl, alcohol and unsaturation regions of 0.9IIR upon accelerated heat aging is presented in Fig. 1 (100, 90, 80 °C) and Fig. 2 (70 °C). At high

temperatures, the functional group development is identical to what was observed with the PIB homopolymer [1], with the exception of the product evolution seen in the carbonyl region at 70 °C for early aging times. In Fig. 2, the early aging of 0.9IIR shows the development of bands at 1709 and 1726  $\text{cm}^{-1}$  up to about 91 days. Afterwards, these peaks are overridden by strong vibrations occurring at 1730 and 1704  $\text{cm}^{-1}$  which have been attributed to ketone and carboxylic acid formation in PIB. As these peaks, along with the 1832  $\text{cm}^{-1}$   $\beta$  lactone are due to thermo-oxidation of the isobutylene units, it is likely that the new bands are related to the oxidation of the isoprene containing regions of IIR. At lower testing temperatures, the development of these new peaks is clearly observed (see Fig. 3). A vibration at approximately 1709  $\text{cm}^{-1}$  grows slowly in magnitude with aging time with a small shoulder appearing later in the 1720–25  $\text{cm}^{-1}$  range. A peak at 1682  $\text{cm}^{-1}$  due to  $\alpha$ ,  $\beta$  unsaturated ketones also becomes visible as a minor component. As no evidence of vinylidene formation (3070 and 882  $\text{cm}^{-1}$ ) was detectable for the 40 and 50 °C aging data, the unsaturated ketone generation can be safely associated with the oxidation of the isoprene units. The  $\beta$  lactone peak also appears to coincide with the growth of the shoulder region of the carbonyl region (1730  $\text{cm}^{-1}$ ) suggesting that thermo-oxidation of the isobutylene rich regions is taking place. The carbonyl growth centered about the peak at 1709  $\text{cm}^{-1}$  can be initially assigned to a carboxylic acid group. Compared to PIB thermo-oxidation, this peak has shifted to higher wavenumbers by about 5  $\text{cm}^{-1}$  suggesting a different structural environment.  $\beta$ -lactone growth is observed but to a much lesser degree than in PIB. Hydroxyl group formation is minimal in the low temperature regime. Isoprene incorporation has changed the profile of oxidation products in IIR versus PIB as seen from 23 to 70 °C.

The functional group development upon heat aging 1.85IIR in the 80–100 °C temperature range (Fig. 4) is quite similar to that observed of 0.9IIR (Fig. 1). Oxidative chemical products are likely similar in spite of the higher isoprene content. The carbonyl region is again dominated by the appearance and growth of the 1730  $\text{cm}^{-1}$  ketonic peak including all other products normally associated with PIB oxidative degradation. The main oxidative products are emanating from the isobutylene regions at higher temperatures.

The 70 °C FTIR aging data for 1.85IIR is showing a more pronounced effect of the early stages of oxidative product development compared to 0.9IIR as displayed in Fig. 5. This is attributed to its higher isoprene content. The 1709  $\text{cm}^{-1}$  oxidation product is strongest in the carbonyl region up to 144 h of aging, thereafter overtaken by the rapid development of the 1730  $\text{cm}^{-1}$  peak. This point in the oxidation process was taking place at about 77 h for 0.9IIR. At longer aging times, the array of vibrational bands becomes quite similar to those of Fig. 4.

The carbonyl region development from room temperature to 60 °C in Fig. 6 corroborates with the short time oxidation processes seen at 70 °C for 1.85IIR as well as with the 0.9IIR observations in Fig. 3. No appreciable oxidative product development was observed outside of the carbonyl region. The early appearance of the 1709  $\text{cm}^{-1}$  peak indicates the importance of this oxidative product during the early stages of IIR degradation. Its development along with the 1682  $\text{cm}^{-1}$  band is higher in concentration compared to the data seen with 0.9IIR for similar aging times, again suggesting that it is emanating from the oxidized isoprene containing zones of the IIR.

Ammonia gas treatment of the 40 °C aged 1.85IIR sample as shown in Fig. 7 caused the loss of the 1709  $\text{cm}^{-1}$  and the development of a broad peak centred at 1560  $\text{cm}^{-1}$ . This confirms that this oxidation peak is a carboxylic acid since it was easily converted to the corresponding carboxylate in reaction with ammonia. This reaction did not affect the 1682  $\text{cm}^{-1}$  peak and

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