

CHARACTERIZATION OF ISOMERIC ELASTOMERS USING THERMAL ANALYSIS

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Abstract

Many of the isomers of polybutadiene and polyisoprene elastomers can be characterized by thermal analysis. T_g is sensitive to side chain units (1,2 or 3,4 structure) for both polymers. Crystallinity measurements can characterize *cis* and *trans* isomers. DMA and DEA master curves provide an idea of the heterogeneity of the chain units from the width of the loss factor curves in the T_g region. Thermal and thermooxidative degradation, as followed by DSC and DTG, can differentiate specific natural and synthetic isomers of polyisoprenes in raw and vulcanized states.

Keywords: characterization, *cis*-, *trans* isomers, crystallinity, DEA, degradation, DMA, DSC, DTG, enthalpy, glass transition temperature, isomers, vinyl

Introduction

Isomeric elastomers are composed of the same chemical elements in the same proportion by weight but differ in structure (arrangement of the atoms or radicals along the polymer back bone). Thus, polyisoprene can occur in the following isomeric structure:

(1) *Cis*-1,4-polyisoprene (NR, IR, guayule rubber); (2) *trans*-1,4-polyisoprene (gutta-percha, balata); (3) Polyisoprenes with vinyl 1,2 and (4) vinyl 3,4 structure (IR).

In addition, NR and IR both are almost 100 percent *cis*-1,4-polyisoprene but differ in the nature of nonrubber constituents and therefore some properties.

Similarly, polybutadiene (BR) can exist in theory in *cis*-1,4, *trans*-1,4, vinyl 1,2, or vinyl 3,4 structures. However, 1,2 and 3,4 structures for BR are identical. The side chain for BR is therefore referred to as vinyl 1,2-units. Again, the BR side chain units can have *isotactic*, *syndiotactic* and *atactic* conformations, depending on the type of catalyst used in their manufacture.

The objective of the present paper is to illustrate, from the information available in published literature that thermal analysis can characterize the above isomeric polymers for both NR and BR.

Discussion

Thermal analysis techniques used in this study are mostly DSC, TG-DTG, DMA and DEA. This does not imply other techniques, such as TMA, TSC-RMA cannot be applied to characterize the isomers of BR and NR. Only, no published literature is available, to the authors' knowledge, to illustrate their usefulness.

Glass transition temperature by DSC

Polybutadienes

Polybutadienes prepared with different catalyst systems differ in relative degree of branching (vinyl-1,2 structure) [1]. Bahary *et al.* [2] assumed that a polybutadiene chain is a terpolymer of *cis*-1,4, *trans*-1,4, and vinyl-1,2 isomers. They used the general equation proposed by Dimarzio and Gibbs [3] for glass transition temperature (T_g) of the polymer and T_g 's of the three homopolymers. The equation takes the form:

$$C[T_g - T_g(cis)] + T[T_g - T_g(trans)] + V[T_g - T_g(vinyl)] = 0, \quad (1)$$

where C , T , and V denote the weight fractions of *cis*-1,4, *trans*-1,4, and vinyl-1,2 groups respectively, and $T_g(cis)$, $T_g(trans)$, and $T_g(vinyl)$ stand for T_g 's of the respective homopolymers. By substituting the values $T_g(cis) = -106 = T_g(trans)$, and $T_g(vinyl) = -15^\circ\text{C}$, Eq. (1) reduces to

$$T_g = 91V - 106 \quad (2)$$

According to Eq. (2), T_g is essentially determined by vinyl content of polybutadiene. Figure 1 shows that T_g and vinyl content of polybutadiene display a linear relationship. The relationship is good considering the presence of *trans* crystallinity in some of the samples. Thus it is possible to estimate vinyl content of polybutadienes from their T_g values.

Equation (2) was further fine tuned to study the effect of steric configuration. Ni *et al.* [4] observed that with the increase of *syndiotactic* 1,2-units, the location of the DMA loss peak shifts to higher temperature and the peak height decreases. Fig-

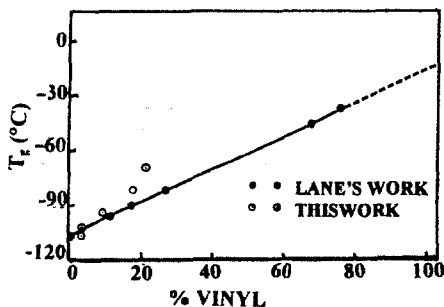


Fig. 1 Relationship between T_g and vinyl contents of polybutadienes

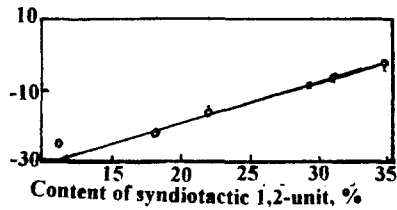


Fig. 2 Relationship between T_g and the content of syndiotactic units in polybutadienes

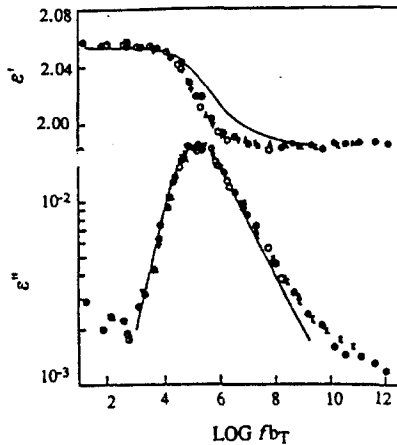


Fig. 3 Master curves of the 1,2-polybutadiene sample with a reference temperature of 296 K: (●) -25°C ; (×) -20°C ; (○) -15°C ; (Δ) -10°C ; (◊) -5°C ; (◊) 0°C ; (◊) 5°C ; (◊) 10°C ; (◊) 15°C ; (◊) 25°C

ure 2 shows that T_g vs. the content of *syndiotactic* 1,2-units follows a linear relationship that can be expressed by a modification of Bahary's [2] relationship as follows:

$$T = 91V + 100S - 106 \quad (3)$$

Here V and S indicate the contents of vinyl-1,2-units and *syndiotactic* 1,2-units, respectively. Equation (3) implies that the *isotactic* sequences possess a less restricted segmental mobility than do the *syndiotactic* sequences.

Determining heterogeneity of microstructure of BR

Figure 3 presents the master curve for dielectric loss vs. shift factor of BR sample of the following microstructure: total 1,2-units 82%, *syndiotactic* 41%, *atactic* 41%, and *isotactic* 18%. The solid line represents the data calculated from the Havriliak-Negami model [5] of relaxation time distributions of this sample. The half-height width of the glass transition, estimated from the loss peak in Fig. 3 is about four decades of frequency and is longer than the usual 1.7 to 2.5 decades for most amorphous polymers [6]. The wider distribution glass transition means a

wider distribution of relaxation times, which undoubtedly arises from the great variety of polybutadiene chain structures. Ni *et al.* [4] suggested that the sample used can be regarded as a copolymer of five monomers: *cis*-1,4-; *trans*-1,4-; *isotactic* 1,2-; *syndiotactic* 1,2-; and *atactic* 1,2-units. Wide glass transition region is desirable for damping applications, which translates high damping to a wide temperature region.

Polyisoprenes

Literature data [7] indicate that T_g of common NR isomers (synthetic *cis*-1,4-polyisoprene, balata, gutta-percha, synthetic *trans*-1,4-polyisoprene) occurs in a narrow range of temperature, from about 203 K to about 210 K (mid-point value). The values of ΔC_p for NR and IR also lie in a narrow region [8] (0.439 to 0.456 J g⁻¹ K⁻¹). Therefore, T_g is not a good indicator for distinguishing these isomers. On the other hand, 3,4 content in the polyisoprene chain can vary widely depending on the catalyst and T_g increases with the increase of 3,4 content in polyisoprene [9, 10]. The data of Kow *et al.* [10] for T_g of polyisoprenes as a function of microstructure are presented in Table 1. Widmaier and Meyer [9] explain the increase of T_g with the 3,4 content by the steric hindrance from the side-chain vinyl group which stiffens the polymer. However, in view of the three components (1,4-, 1,2-, and 3,4-structures) of the synthetic polyisoprenes, the data can not be fitted to a uniform relationship between the microstructure and T_g in the form of Gordon-Taylor [11] or Fox and Lashack expressions [12].

Table 1 Glass transition temperature of polyisoprene as a function of microstructure^a

Sample	$M_n \times 10^{-3}$ / g mol ⁻¹	[Amine]/ [RLI] ratio	Microstructure/%				T_g / °C ^b	
			1,2	3,4	<i>cis</i> -1,4	<i>trans</i> - 1,4		
NR	—	—	—	—	~100	—	—	-100
HS6PC	139	—	—	7	70	—	23	-68
PI-7	159	80°	—	24	49	—	27	-52
PI-4	173	280°	—	33	37	—	30	-40
PI-3	173	830°	~1	45	28	—	25	-34
PI-9AA	151	60 ^d	15	55	—	30	—	-9
PI-8AA	108	220 ^d	18	70	—	12	—	-2
PI-EF-2	72	5°	20-25	70-75	—	~1	—	12

^a From Kow *et al.* [10]; ^b Extrapolated value; ^c Triethylamine;

^d Tetramethylene ethylene diamine; ^e bis-piperidine ethane

Crystallinity

Polybutadienes

Different polybutadiene rubbers differ in crystallinity that can be followed by DSC. Crystallinity has been observed in all BR isomers [2]: high *cis*, high *trans*, high vinyl. An increased melting temperature (T_m) is observed as either *cis* or *trans*

content in the corresponding polybutadiene increases. The melting point depression of a crystalline random copolymer has been described by Flory [13] as:

$$1/T_m = 1/T_m^0 - (R/\Delta H_m)\ln X, \quad (4)$$

where T_m is the melt temperature in K; T_m^0 is the equilibrium melting point of the pure polymer; R , the gas constant; ΔH_m , the heat of fusion; and X the mole fraction of either *cis* or *trans* units. A plot of $1/T_m$ vs. negative logarithm of the mole fraction of *trans* units shows two discontinuous straight lines, corresponding to the α and β forms of *trans* polybutadiene. The plot for *cis* BR is presented in Fig. 4. The melting point of the pure *cis* BR by extrapolation in Fig. 4 is 4°C. This value is in good agreement with literature values [14, 15]. Estimated heat of fusion for *cis* BR from Fig. 4 is 2.511 kJ mol⁻¹, assuming a random distribution of structural imperfections.

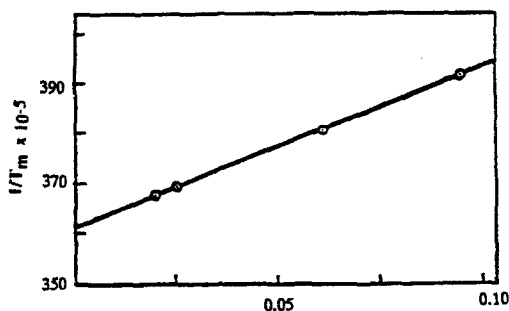


Fig. 4 Inverse melt temperature as a function of *cis* content of polybutadienes

Polyisoprenes

The high *cis*-1,4 polyisoprene (IR) is structurally similar to NR. There are, however, important differences in properties, both physical and chemical [16]. One of the important differences in physical property is crystallizability, which gives rise to outstanding green strength of NR.

The relationship between the microstructure and crystallinity, as derived from ΔH_m , shows an increase of crystallinity with *cis* content of IR. NR has outstanding crystallinity at short crystallization times. However, with prolonged crystallization (163 h at 239 K) there was not much difference between NR and seven titanium-aluminum catalyzed IR samples [17]. Considerable variation for different IR samples at short crystallization times indicates that the most prominent difference between NR and IR samples is in the rate of crystallization and not in the final crystallinity. Interestingly, Chen *et al.* [18] used birefringence to determine crystallinity of IR and observed that the enhancement of green strength of IR correlates with the increase of crystallization rate through introduction of additives.

A DTA study of *trans*-1,4 polyisoprene [19] exhibits four endothermic melting peaks between 30 and 70°C (with ΔH_m somewhat higher than NR). Burfield and

Eng [20] reported a T_m of 325 K and $\Delta H_m=74.1 \text{ J g}^{-1}$. This compares with values of $T_m=277 \text{ K}$ (determined at the onset of melting instead of the peak temperature cited in the literature) and $\Delta H_m=25.5 \text{ J g}^{-1}$ for NR samples crystallized under optimum conditions [21].

Methods based on oxidation of elastomers

Polyisoprenes

DSC enthalpy of the oxidative degradation of elastomers provides the value of the peak temperature T_p and also the area under the peak. Goh [22] suggested that DSC exotherms in oxygen can be applied to distinguish between the natural and synthetic polyisoprenes in the raw stage. Both peak temperature and exotherm area are characteristic of the type of polyisoprene as shown in Fig. 5 (note that the exotherms are pointing downward). The peak temperatures for the natural isomers (NR, 220°C; gutta-percha, 184°C) are higher than those for corresponding synthetic counterparts (IR-167°C, Transp-167°C). This was ascribed to the presence of naturally occurring antioxidants in NR (conferring stability) and to the catalytic effect of the metallic oxides present in the synthetic products on their oxidation.

The heats of oxidation for both NR and gutta-percha are also higher than those for the synthetic counterparts. A small size (0.5–0.7 mg) and solution cast samples were used in this investigation to improve thermal contact between the sample and the DSC pan. The heats of oxidation are: NR, 2680 J g⁻¹; IR, 1535 J g⁻¹; gutta-percha, 1585 J g⁻¹; and Transp 100, 1510 J g⁻¹. These values are much higher than those reported previously [23], showing the importance of thermal contact.

Thermal degradation in nitrogen

Polymers when heated in nitrogen normally degrade by breaking down to smaller fragments, which subsequently volatilize. Contrary to this expectation, thermal degradation of IR, BR, SBR, and to some extent NR, show exothermal curves in DSC experiments under nitrogen.

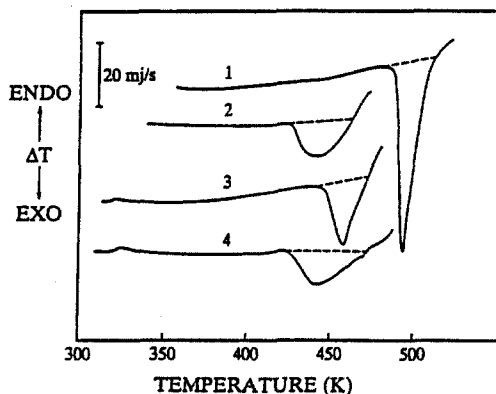


Fig. 5 DSC curves of various polyisoprenes in oxygen: (1) NR, 0.74 mg; (2) Natsyn 2200, 0.62 mg; (3) gutta-percha, 0.68 mg; (4) Transp 100, 0.68 mg

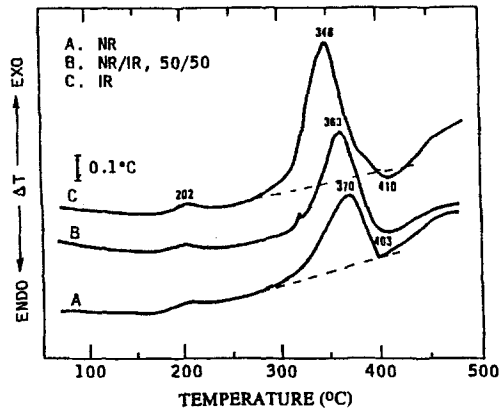


Fig. 6 DSC thermal degradation curves of NR and IR compounds. (A) 14.90 mg; (B) 14.22 mg; (C) 14.20 mg

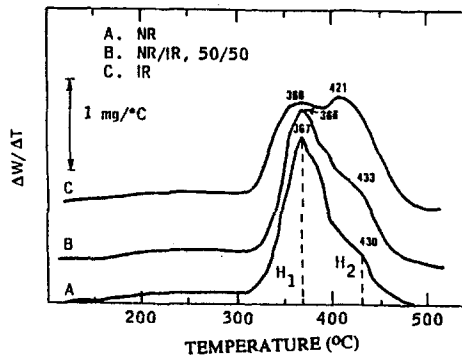


Fig. 7 DTG thermal degradation curves of NR and IR compounds. (A) 9.29 mg; (B) 9.87 mg; (C) 9.85 mg

The methods described so far for distinguishing NR and IR relate to raw elastomers. Sircar and Lamond [24, 25] as well as Brazier and Nickel [26] proposed the use of DSC and DTG thermal degradation curves of these elastomer to characterize them in the vulcanized state. In essence, the methods is based on the observation that sulfur-cured, carbon black-reinforced IR and NR exhibit significantly different DTG and DSC curves in nitrogen. However, the raw elastomers and peroxide cured gum vulcanizates have identical thermal degradation curves. Figure 6 shows that the exotherm area for IR vulcanizate is much larger than that for NR.

DTG of these same compounds (Fig. 7) shows that the IR system has two sharp peaks (370 and 420°C), whereas the NR system has a sharp 370°C peak and an inflection near 430°C. The cross-linked and cyclized network (corresponding to the larger DSC exotherm area) degrades at a higher temperature; this accounts for the second DTG peak for IR. The NR and IR blends were intermediate.

Confirmation of the above explanation was provided by Gelling *et al.* [27] who isolated a much greater amount of substituted aromatic (cyclized) product from vulcanized IR than from NR, especially in the presence of carbon black. Also, when most of the catalyst residues in IR are removed by filtration, the DTG of the degraded products simulates that of NR. On the other hand, cyclized NR shows only the second DTG peak, corresponding to final degradation of IR. Figure 8 shows the characteristic degradation patterns for carbon black-filled vulcanizates of NR, IR (Natsyn 2200), purified IR, and cyclized NR, which confirm the above observations.

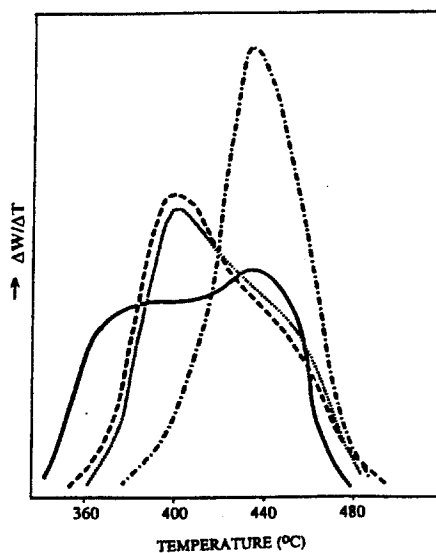


Fig. 8 DTG curves of black filled vulcanizate of NR (----) Natsyn 2200 (—) and purified Natsyn 2200 (.....), compared with cyclized NR (- · - · -). The recipe consists of rubber (NR or IR), 100, HAF black, 50; ZnO, 5; stearic acid, 2; CBS, 0.6; sulfur, 2.5 - cured at 140°C for 40 min

Further work by Gelling *et al.* shows different DTG degradation patterns for IR produced by Ziegler-Natta vs. lithium alkyl catalysts. Lithium compounds are more effective in causing cyclization than aluminum and titanium. Only minor differences are observed between unvulcanized NR and Natsyn 2200, either with or without carbon black. Thus, the differences become marked only after vulcanization. Gelling *et al.* [27] concluded that, in view of the complex interactions, more comprehensive studies on the effect of other vulcanizing systems and additives would be recommended.

Conclusions

1. Polybutadienes and polyisoprenes with side chain units can be characterized using glass transition temperature.

2. The half-width of the dynamic mechanical and dielectric loss factor master curves in the T_g region gives a measure of the heterogeneity of BR vinyl-1,2-units.

3. *Cis* and *trans* isomers for both polyisoprene and polybutadiene can be characterized by their crystalline melt temperatures and enthalpy values.

4. DSC enthalpy and peak temperature of the oxidative degradation of elastomers provide information to identify natural and synthetic polyisoprene isomers in the raw stage.

5. Finally, natural rubber and synthetic *cis*-1,4-polyisoprene vulcanizates can be characterized by using DSC and DTG thermal degradation curves.

Thus, thermal analysis is a useful tool to characterize BR and NR isomers.

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