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(22) The reported $[\alpha]_D$ for optically pure 2-methylbutylamine is higher than that reported by Goodman and Chen (ref 7). See: Newman, P. "Amine and Related Compounds", In *Optical Resolution Procedures for Chemical Compounds*; Manhattan College Publications: Riverdale, NY, 1981; Vol. 1, p 35-36. Although their (ref 7) optical purity is 71%, one cannot simply correct the molar ellipticity because of the unknown stereoelection factor in the polymerization; $\phi = 13000$ is therefore a minimum value.
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Regioselectivity in Isoprene Inclusion Polymerization

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ABSTRACT: Polyisoprene obtained by radiation polymerization in perhydrotriphenylene clathrates possesses a pure 1,4-trans structure but contains a significant number of head-to-head, tail-to-tail defects. Triad and tedrad sequences are detected in the ^{13}C NMR spectrum: their distribution is interpreted as a succession of direct and inverted units. Probability parameters and their temperature coefficients are determined both in a Bernoullian approximation and as a first-order Markov chain.

In the past few years we have pointed out several times the high degree of regularity existing in polymers obtained by radiation polymerization in perhydrotriphenylene (PHTP) clathrates,[1-4] the only notable exception being polyisoprene. A 1,4-trans structure was assigned to this polymer on the basis of the IR spectrum;[5] however on

X-ray analysis it appears as an amorphous product, in contrast with the already known natural and synthetic 1,4-*trans*-polyisoprene, which is crystalline and melts at about 65 °C.[6]

The polymer structure was recently clarified through its ^{13}C NMR spectrum at 25.2 MHz:[7,8] it shows a high degree of chemical and steric regularity (only 1,4-trans units are present) but contains a significant number of head-to-head, tail-to-tail sequences besides the prevailing head-to-tail junctions. This fact is fully consistent with the general behavior observed in the PHTP inclusion polymerization of substituted butadienes.[4,8] From among the investigated monomers isoprene only possesses the two necessary characteristics in order for this type of defect to be produced and detected: the absence of substituents in the terminal positions (bonded to carbons C1 or C4) and the presence of substituents in an internal position (on carbons C2 or C3) in such a way as to lower the symmetry of the monomeric unit.

In this paper we present a detailed analysis of the microstructure of polyisoprene samples produced by inclusion polymerization in PHTP, with special concern for the sequence distribution. We also examine the possibility of controlling the number of defects by a proper choice of experimental conditions.

Experimental Section

Perhydrotriphenylene (PHTP) was synthesized and purified according to already reported procedures.[9] Isoprene (a Fluka purum product) was used after distillation.

Polymerization was carried out by using the technique of preirradiated matrix.[10] Pure monoclinic PHTP (~5 g) was irradiated under vacuum in glass vials equipped with a breakable seal (^{60}Co γ-ray source, dose 0.5 Mrad, room temperature). After careful degassing of both monomer and irradiated PHTP, an isoprene excess (~1.5 mL) was introduced through a vacuum line in the vials cooled in liquid nitrogen. Monomer and matrix were put in contact at a fixed temperature (from −60 to +70 °C) and maintained at that temperature for a time ranging from 1 h (at +70 °C) to 1 week (at −60 °C). The vial content was extracted with boiling MeOH until the complete dissolution of the host. Polyisoprene was purified by dissolution in $CHCl_3$ and precipitation in excess MeOH. Molecular weights were intentionally kept low (3000–5000) in order to avoid solubility troubles; they were determined by viscometry in benzene at 32 °C.[11]

^{13}C NMR spectra were recorded at 50.3 MHz with a Varian XL-200 instrument under the following conditions: concentration, 2–8% (w/v); acquisition time, 1.3 s; pulse angle, 25°; 32 000 points over 12 000 Hz; 5000–40 000 transients. For quantitative measurements the following conditions were used: acquisition time, 1.6 s; delay time, 10 s; pulse angle, 90°; decoupler switched on only during acquisition time in order to suppress the nuclear Overhauser effect.

DSC curves were obtained by a TA 3000 Mettler instrument.

Analysis of the ^{13}C NMR Spectra

The ^{13}C NMR spectra of the investigated polyisoprene samples consist of five groups of peaks, corresponding to the five carbon atoms of the constitutional repeating unit. The chemical shift of the main peak of each group agrees with that predicted for the presence of 1,4-trans units. Two of these groups, those corresponding to the saturated metylene carbons C1 and C4, when examined at 15–25 MHz, appear to be formed by two well-separated signals ($\Delta\nu \simeq$ 1.2–1.5 ppm). The intensity ratio inside each pair of signals varies with the polymerization temperature and ranges between 1:6 and 1:2.

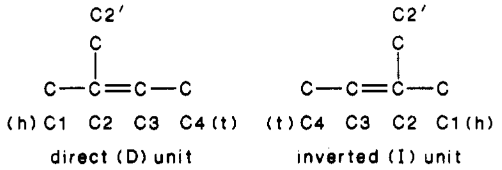
This splitting was interpreted as an indication of the presence of a notable amount of head-to-head, tail-to-tail junctions, in addition to the prevailing head-to-tail ones. This conclusion was achieved by comparison with literature data[12,13] and by an analysis performed with the use of an additive parameter set that is valid for a wide series of methyl-substituted 1,4-*trans*-polybutadienes.[8,14] No evidence of other structures, such as 1,4-cis, 1,2-, or cyclic units, is observed in the spectrum, even when recorded with a high signal-to-noise ratio.

Table I
50.3-MHz ^{13}C NMR Spectrum of 1,4-*trans*-Polyisoprene

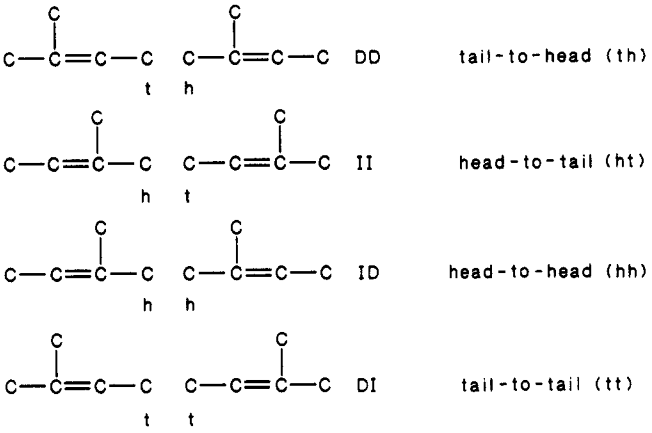
peak	chem shift, ppm from Me_4Si[a]	assignt carbon	sequence
A	16.03 (15.99)	C2′ (CH_3)	
B	26.73	C4 (CH_2)	ht
C	28.29	C4 (CH_2)	tt
D	38.49 (38.53)	C1 (CH_2)	hh[b]
E	39.75	C1 (CH_2)	ht
F	124.23 (124.17)	C3 (—CH=)	
G	134.93	C2 (—C(CH_3)=)	ht,ht
H	135.06	C2 (—C(CH_3)=)	ht,hh[b]
I	135.11	C2 (—C(CH_3)=)	tt,ht[b]
L	135.24	C2 (—C(CH_3)=)	tt,hh

[a] Minor components are in parentheses. [b] See text.

In the following analysis we shall use the convention of indicating the monomeric units having carbon C1 at the left or at the right direct (D) or inverted (I), respectively.



Carbon C1, which is nearer than C4 to the substituent, is considered as the head of the monomer unit. The possible diads are



DD and II diads, corresponding to tail-to-head and head-to-tail sequences and differing only in the sense of observation, cannot be distinguished in the spectrum. The adjacent methylene carbons are anisochronous in ht sequences as they correspond to carbons C1 and C4, but isochronous, at least at the diad level, in hh (C1 and C1) and tt (C4 and C4). Regioselectivity evaluation can easily be obtained from the spectrum. With reference to Figure 1 and Table I, *B*, *C*, *D*, and *E* being the intensities of the four peaks normalized over the single carbons and the chain continuity condition *C* = *D* having been taken into account, the sequence concentration is expressed by

$$(\mathrm{ht}) = B = E \qquad (1)$$

$$(\mathrm{hh}) = (\mathrm{tt}) = C/2 = D/2 \qquad (2)$$

Under our experimental conditions (hh) and (tt) concentrations range between 7 and 16%.

The analysis of sequence distribution requires a knowledge of chain segments longer than diads and hence

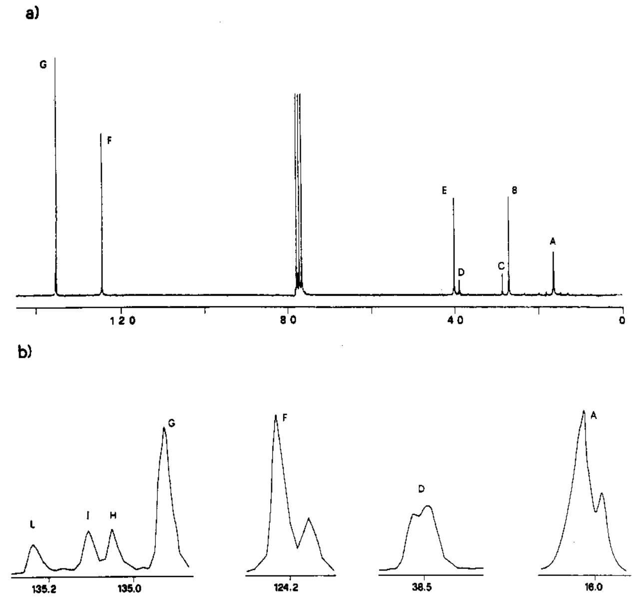
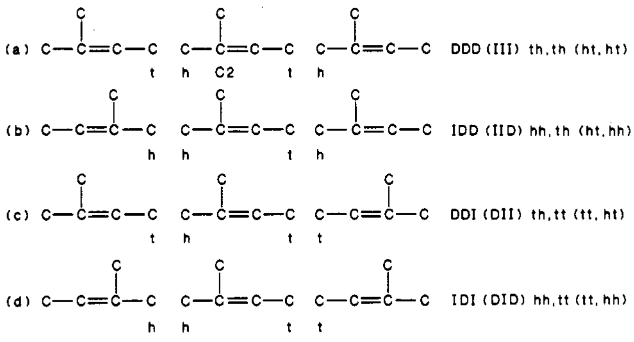


Figure 1. ^{13}C NMR spectrum of polyisoprene recorded at 50.3 MHz: (a) full spectrum of the sample synthesized at -40 °C; (b) fine structure of carbons C2, C3, C1 (h,h), and C2′ (from the left) in the sample synthesized at +40 °C. All peaks are recorded on the same scale.

the use of spectrometers operating at higher frequency. The gain in resolution obtained at 50.3 MHz permits a quantitative triad evaluation and gives evidence of signal splitting attributed to tetrads of monomeric units (Table I).

Peaks A (corresponding to the methyl group C2′) and F (C3) appear split into a major and a minor component (Figure 1b), but the most relevant feature of this spectrum is the presence of three weak peaks around 135 ppm, downfield from the main peak C2 (Figure 1b), in agreement with a triad sensitivity.



According to the scheme developed by our group for 1,4-*trans*-polybutadienes,[8] the chemical shift of the observed carbon atom may be expressed in terms of additive contributions due to methyls substituted in positions α, β, γ, etc., as reported in detail in ref 8. In particular the chemical shift of the C2 carbon in each sequence can be written, respectively

$$\mathrm{C2(ht,ht)} = \text{constant term} + T + \delta_T + \delta_T'$$

$$\mathrm{C2(ht,hh)} = \text{constant term} + T + \gamma_T + \delta_T'$$

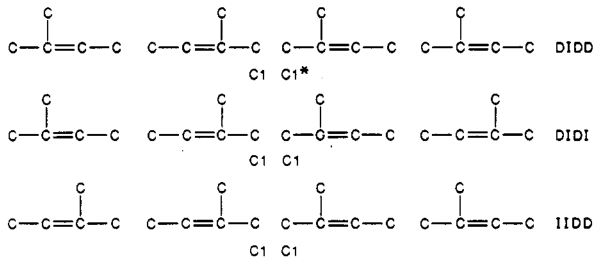
$$\mathrm{C2(tt,ht)} = \text{constant term} + T + \delta_T + \epsilon_T'$$

$$\mathrm{C2(tt,hh)} = \text{constant term} + T + \gamma_T + \epsilon_T'$$

Supposing none of such values were known, assignments can be deducted in a pure logical way. The ht,ht sequence (a) (corresponding to triads DDD and III) was assigned to peak G because it is the most intense peak. Since it is placed upfield with respect to the other signals, it means that (b) > (a) (as expressed in ppm) and (c) > (a). We deduce, therefore, that $\gamma_T > \delta_T$ and $\epsilon_T' > \delta_T'$. As a consequence, the structure whose equation contains the largest parameters (d) and corresponds to the tt,hh sequence (IDI and DID) must be attributed to the peak downfield, i.e., L.

A definite assignment of peaks H and I (differing by 0.05 ppm) to the ht,hh or tt, ht sequences has not yet been made. We tried to solve this problem by comparing our spectrum with that of squalene, a triterpene containing ht,ht and tt,ht 1,4-*trans*-isoprene sequences. Its spectrum recorded at 50.3 MHz, as recently reported by Schilling et al.,[15] shows resolved peaks for all 15 independent carbon atoms. A slight preference toward the assignment of peak I to tt,ht sequences was obtained, but this conclusion is not fully reliable, due to the inadequacy of the model at this level of accuracy. In any case this ambiguity has no effect on the structural and mechanistic considerations since the two sequences are necessarily present in equal amounts. Incidentally, the comparison with the polymer led to further assignments in the spectrum of squalene itself.[16]

A further remark of the polyisoprene spectrum concerns the splitting observed in the methylene signal at 38.5 ppm, corresponding to hh sequences (C1 in the ID diad) (Figure 1b). This splitting should be attributed to the different tetrads centered on the ID diad. Only three distinguishable tetrads of this type exist, DIDD (or its equivalent IIDI), DIDI, and IIDD



The two central C1 carbons of both tetrads DIDI and IIDD are isochronous, related by a symmetry operation; instead, in DIDD they are heterotopic (C1 and C1*) and can possess a different chemical shift. Four signals can thus be expected in the corresponding spectral region. However, differences in the structure are so far from the nucleus under observation that some of these signals are not resolved under our experimental conditions. By considering only α', β, and ϵ' contributions, as done in our previous paper,[8] we obtain the following equations:

$$\mathrm{C1\ (DIDD)} = \text{constant term} + \alpha' + \beta$$

$$\mathrm{C1^*\ (DIDD)} = \text{constant term} + \alpha' + \beta + \epsilon_\alpha'$$

$$\mathrm{C1\ (DIDI)} = \text{constant term} + \alpha' + \beta$$

$$\mathrm{C1\ (IIDD)} = \text{constant term} + \alpha' + \beta + \epsilon_\alpha'$$

Under these limitations C1 in DIDD should almost coincide with C1 in DIDI and C1* in DIDD with C1 in IIDD. DIDD is certainly the most abundant tetrad and the difference in probability between DIDI and IIDD is small; as a consequence, the two peaks should have almost the same intensity, in agreement with the experiment.

Head-to-head, tail-to-tail sequences were recognized at the diad level in polychloroprene[17] and in polyisoprene obtained with alfin catalyst[12] and at the tetrad level in poly(vinylidene fluoride),[18] where, however, the monomeric units possess only two carbon atoms in the chain. In our case, the sensitivity extends over a chain segment 12–15 bonds long and is quite exceptional as only very few counterparts are found in the literature.[19,20]

A Probabilistic Approach

We treated polyisoprene as a copolymer of two pseudomonomers, one corresponding to the direct (D or 1,4) unit and the other to the inverted (I or 4,1) unit. We can express the monomer distribution as a first-order Markov chain by using two conditional probabilities, p_{ID} and p_{DI}.

The frequencies of the four diads are

$$\mathrm{DD} = F_{\mathrm{D}}(1 - p_{\mathrm{DI}}) \qquad \mathrm{ID} = (1 - F_{\mathrm{D}})p_{\mathrm{ID}}$$

$$\mathrm{DI} = F_{\mathrm{D}}p_{\mathrm{DI}} \qquad \mathrm{II} = (1 - F_{\mathrm{D}})(1 - p_{\mathrm{ID}})$$

The analytical concentration of the sequences is

$$(\mathrm{ht}) = \mathrm{DD} + \mathrm{II} = F_{\mathrm{D}}(1 - p_{\mathrm{DI}}) + (1 - F_{\mathrm{D}})(1 - p_{\mathrm{ID}})$$

$$(\mathrm{hh}) = \mathrm{ID} = (1 - F_{\mathrm{D}})p_{\mathrm{ID}}$$

$$(\mathrm{tt}) = \mathrm{DI} = F_{\mathrm{D}}p_{\mathrm{DI}}$$

For the high molecular weight polymer the following stoichiometric relations should hold:

$$(\mathrm{hh}) = (\mathrm{tt}) \qquad F_{\mathrm{D}} = p_{\mathrm{ID}}/(p_{\mathrm{ID}} + p_{\mathrm{DI}})$$

where F_{D} is the mole fraction of D units in the chain.

Taking into account the spectral assignments reported in the previous section, we obtain

$$(\mathrm{ht}) = 1 - 2p_{\mathrm{ID}}p_{\mathrm{DI}}/(p_{\mathrm{ID}} + p_{\mathrm{DI}}) = B = E \tag{3}$$

$$(\mathrm{hh}) = (\mathrm{tt}) = p_{\mathrm{ID}}p_{\mathrm{DI}}/(p_{\mathrm{ID}} + p_{\mathrm{DI}}) = C/2 = D/2 \tag{4}$$

Analogously at the triad level we can write

$$\mathrm{DDD} = F_{\mathrm{D}}(1 - p_{\mathrm{DI}})^2 = p_{\mathrm{ID}}(1 - p_{\mathrm{DI}})^2/(p_{\mathrm{ID}} + p_{\mathrm{DI}})$$

$$\mathrm{DDI} = F_{\mathrm{D}}p_{\mathrm{DI}}(1 - p_{\mathrm{DI}}) = p_{\mathrm{ID}}p_{\mathrm{DI}}(1 - p_{\mathrm{DI}})/(p_{\mathrm{ID}} + p_{\mathrm{DI}})$$

etc., and

$$(\mathrm{ht,ht}) = \mathrm{DDD} + \mathrm{III} \qquad (\mathrm{tt,ht}) = \mathrm{DDI} + \mathrm{DII}$$

$$(\mathrm{ht,hh}) = \mathrm{IDD} + \mathrm{IID} \qquad (\mathrm{hh,tt}) = \mathrm{IDI} + \mathrm{DID}$$

from which

$$(\mathrm{ht,ht}) = 1 + p_{\mathrm{ID}}p_{\mathrm{DI}} - 4p_{\mathrm{ID}}p_{\mathrm{DI}}/(p_{\mathrm{ID}} + p_{\mathrm{DI}}) = G \tag{5}$$

$$(\mathrm{ht,hh}) = (\mathrm{tt,ht}) = 2p_{\mathrm{ID}}p_{\mathrm{DI}}/(p_{\mathrm{ID}} + p_{\mathrm{DI}}) - p_{\mathrm{ID}}p_{\mathrm{DI}} = H = I \tag{6}$$

$$(\mathrm{hh,tt}) = p_{\mathrm{ID}}p_{\mathrm{DI}} = \mathrm{L} \tag{7}$$

Comparison of these equations with those of the diads gives

$$(\mathrm{ht}) = (\mathrm{ht,ht}) + (\mathrm{ht,hh}) = (\mathrm{ht,ht}) + (\mathrm{tt,ht})$$

$$2(\mathrm{hh}) = 2(\mathrm{tt}) = (\mathrm{hh,tt}) + (\mathrm{ht,hh}) = (\mathrm{hh,tt}) + (\mathrm{tt,ht})$$

If normalization conditions and stoichiometric relationships ($C = D$, $H = I$, $L + H = C$) are considered, the independent experimental data required for the determination of both p_{ID} and p_{DI} can be obtained from the C2 spectrum (e.g., L and H) or one from C2 (L or H) and one from C1 (D) or C4 (C). When choosing L and H, we obtain

$$p_{\mathrm{ID}} = \frac{L \pm (L^2 - (L + H)^2L)^{1/2}}{L + H} \tag{8}$$

$$p_{\mathrm{DI}} = L/p_{\mathrm{ID}} \tag{9}$$

We should observe that the second solution for p_{ID} corresponds to the first for p_{DI}. The choice between these solutions is not possible on statistical grounds only but requires further independent information. This can be obtained from ESR analysis of the growing chain end in PHTP inclusion polymerization. As already discussed in a recent paper[21] the poly(isoprenyl) spectrum reveals the prevailing presence of a radical having the highest spin density on carbons C2 and C4. This corresponds to a D (or 1,4) insertion

$$\text{—CH}_2\text{C(CH}_3\text{)=CHCH}_2{}^{\bullet}$$

As a consequence we shall use a p_{ID} value greater than p_{DI}.

Table II
Sequence Distribution in 1,4-*trans*-Polyisoprene

	temp, °C					
	+70	+40	+25	−20	−40	−60
			Peak Intensity			
B	0.728	0.768	0.730	0.797	0.824	0.853
C	0.272	0.232	0.270	0.203	0.176	0.147
D	0.317	0.214	0.230	0.203	0.177	0.149
E	0.683	0.786	0.770	0.797	0.823	0.851
G	0.459	0.531	0.550	0.565	0.707	0.780
$H + L$	0.382	0.326	0.310	0.313	0.207	0.150
L	0.159	0.143	0.140	0.122	0.086	0.070
			Probability Parameters			
p_{I}	0.203	0.152	0.161	0.139	0.103	0.080
p_{DI}	0.206	0.154	0.162	0.140	0.103	0.080
p_{ID}	0.702	0.779	0.785	0.736	0.806	0.886
S^a	0.908	0.933	0.947	0.876	0.909	0.966
P^b	1.636	1.558	1.417	2.203	2.096	1.480

[a] $S = p_{\mathrm{ID}} + p_{\mathrm{DI}}$. [b] $P = (1 - p_{\mathrm{ID}})(1 - p_{\mathrm{DI}})/(p_{\mathrm{ID}}p_{\mathrm{DI}})$.

The above reported equations are equivalent with those reported by Wilson[22] and by Koenig,[23] and, apart from a normalization factor, with those reported by Cais and Sloane.[18]

Equations 3–8 may be converted to (3′–8′) if one assumes a Bernoullian distribution of direct and inverted units, i.e., if $p_{\mathrm{ID}} = 1 - p_{\mathrm{DI}} = p_{\mathrm{D}}$ (>0.5).

$$(\mathrm{ht}) = 1 - 2p_{\mathrm{D}}(1 - p_{\mathrm{D}}) \tag{3′}$$

$$(\mathrm{hh}) = (\mathrm{tt}) = p_{\mathrm{D}}(1 - p_{\mathrm{D}}) \tag{4′}$$

$$(\mathrm{ht,ht}) = 1 - 3p_{\mathrm{D}}(1 - p_{\mathrm{D}}) \tag{5′}$$

$$(\mathrm{ht,hh}) = (\mathrm{tt,ht}) = (\mathrm{hh,tt}) = p_{\mathrm{D}}(1 - p_{\mathrm{D}}) \tag{6′, 7′}$$

$$p_{\mathrm{D}} = \frac{1 + (1 - 4L)^{1/2}}{2} \tag{8′}$$

Experimental peak intensities normalized over the single carbons are reported in Table II. From an analysis of the data, the following remarks could be drawn:

(a) Peaks C and D have approximately the same intensity; the same is true for H and I, if the spectrum is sufficiently well resolved.

(b) An optimization of data is required in order to make the experimental values consistent with the other necessary relationships, in particular with $C = L + H$. The discrepancy between the sequence concentration observed on saturated and unsaturated carbons might be related to the low integration accuracy (due to partial signal overlapping), to a different response factor for the single sequences centered on the same carbon, and to the deviation from the infinite chain statistics.

(c) The ratio between L and H is systematically lower than 1.

Evaluation of probability parameters can be performed in different ways, depending on the weight we give to point c.

The statistical analysis was first performed by using eq 3′–7′: the conditional probabilities p_{I} are reported in the Table II. Agreement with the experimental data is satisfactory and a Bernoullian distribution can be accepted as a first-order approximation of the polyisoprene microstructure. However, this interpretation implies a sys-

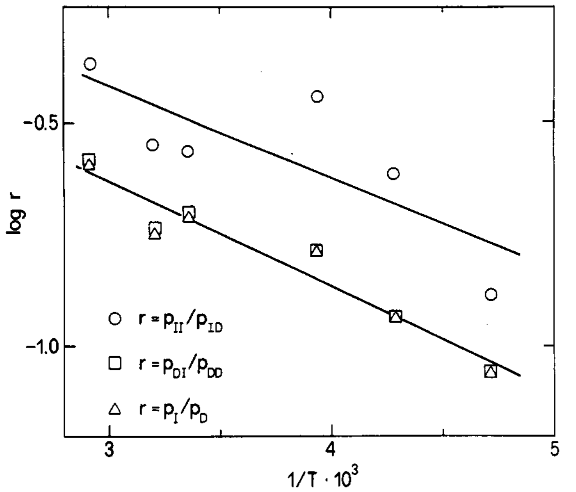


Figure 2. Temperature dependence of regioregularity of polyisoprene.

tematic overestimation of peak L (hh,tt), which is supposed to have the same intensity as H and I (in this case point c is neglected and the difference in peak intensity between L and H is considered within experimental error).

The use of 3–7 (first-order Markov distribution) together with an appropriate statistical weight for the *L*/*H* ratio gives the values of p_{ID} and p_{DI} reported in Table II. As indices of the deviation from the Bernoullian distribution we report in Table II the values S ($=p_{ID} + p_{DI}$) and R ($=p_{DD}p_{II}/p_{ID}p_{DI}$): the first index is always <1 and the second >1. The main difference with respect to the previous case concerns the p_{ID} value, which is markedly lower than p_D, while p_{DI} is almost identical with $1 - p_D$. This indicates a slight trend toward the formation of pairs of inverted units. As an example the number-average length of I units at 25 °C is 1.50 for a first-order Markov chain, compared with 1.20 for a Bernoullian process.

It can be shown that in the concentration range experimentally observed the intensity of peaks B, C, D, E and G depends in practice only on the lower probability parameter (in our case p_{DI}), whereas H, I, and L are affected by both p_{DI} and p_{ID}. This explains why p_{DI} coincides with p_I ($=1 - p_D$) (in the Bernoullian approximation) and why the p_{ID} values are rather scattered, due to the experimental errors in the evaluation of peak L.

The dependence of polyisoprene microstructure on the polymerization temperature was investigated from −60 to +70 °C. Data were interpreted by assuming the validity of an Arrhenius type diagram, where the logarithm of the ratios p_I/p_D, or p_{DI}/p_{DD} and p_{II}/p_{ID} is plotted vs. $1/T$ (Figure 2). The three straight lines are almost parallel to each other and their slopes, expressed as activation energies, have similar values: 4.46 ± 0.62 kJ mol^{-1} for p_I/p_D and 4.55 ± 0.62 and 3.9 ± 1.5 kJ mol^{-1} for p_{DI}/p_{DD} and p_{II}/p_{ID}, respectively. From this point of view too, our system does not deviate greatly from a purely random succession of opposite units.

Extension of the polymerization range toward higher and lower temperatures meets with thermodynamic and kinetic difficulties. At higher temperatures the PHTP monomer clathrate decomposes and polymerization cannot occur any more.[2,4,24] At lower temperatures the polymerization rate becomes too low for preparative purposes.

As already mentioned, polyisoprene obtained in PHTP clathrates in ordinary conditions is amorphous. Only the samples obtained at low temperature (−60 °C), due to their lower content of regioisomeric defects, show a weak endothermal transition around 35–40 °C in the DSC curve. The intensity of the peak increases after long annealing at 5 °C and reaches at the most 40 J g^{-1}. In any case the crystallinity degree calculated by comparison to the literature data for pure head-to-tail 1,4-*trans* polyisoprene is quite small.

Registry No. Polyisoprene, 9003-31-0.

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