Table I
Comparison of Predictions of the Dissociable Junction Model with Experiment

expt no.	dose, eV/g × 10^{-20}	$\nu_{1e} \times 10^4$	Φ	$\nu_x \times 10^4$	λ_0	λ_s predicted	λ_s exptl
C236	2.3	0.85	0.47	1.82	1.556	1.235	1.098
C230	3.8	1.85	0.114	16.2	1.535	1.443	1.145
C255	4.5	2.15	0.042	51	1.370	1.348	1.091

junction model and experiment and it has very little effect on a plot such as Figure 1.)

The relation between λ_s and λ_0 for the dissociable junction model was calculated as follows. For a given pair of ν_e and ν_{1e}, a value of Φ was assumed and ν_x was calculated from eq 2; ϕ_2 was obtained from eq 4, and a revised value of Φ was obtained from eq 36 of ref 4. The process was iterated to a constant value of Φ, and then λ_s was calculated as a function of λ_0 from eq 2–4. An example is shown in Figure 1 for 1,2-polybutadiene with $\nu_e = 2.41 \times 10^{-4}$ mol/cm^3, $\nu_{1e} = 2.15 \times 10^{-4}$ mol/cm^3.[6] If the junctions dissociated leaving no trace in the configuration of the network, there would be no retraction after release and λ_s would equal λ_0 as shown by the dashed line. In fact, there is a predicted retraction to a state of ease $\lambda_s < \lambda_0$, due to the memory effect, but it is small, of the order of 10%. On the same graph, an experimentally determined point is shown for $\lambda_0 = 1.370$, and the actual retraction is much greater.

Numerical results for this and two other experiments are given in Table I. The 1,2-polybutadiene was the same identified as polymer C in earlier publications;[3,5] cross-linking was performed by γ irradiation at −10 °C as previously described[5] with the doses indicated. The strand concentrations ν_{1e} and ν_x are given in mol/cm^3. In every case the observed λ_s is much smaller than that predicted from the dissociable junction model; the memory effect does not account for the magnitude of the retraction.

It may be added that the values of ν_x in Table I are unrealistically large and would imply a Young's modulus for extension of the final network from the state of ease far larger than that observed. By contrast, the trapped entanglement model provides a prediction for the stress–strain relation in extension from the state of ease that agrees precisely with experiment.[5] It can be concluded that the properties of the networks cross-linked in strained states do confirm the presence of permanently trapped entanglements (or equivalent trapped topological restraints).

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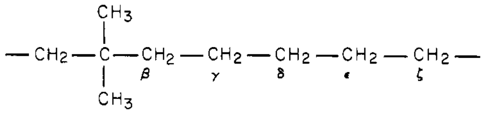
Communications to the Editor

Cationic Copolymers of Isobutylene. 4. Heptad and Octad ^{13}C NMR Signals in Isobutylene-*trans*-1,3-Pentadiene Copolymers

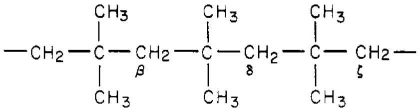
During previous investigations on the structure and the monomer distribution of copolymers based on isobutylene (I) and conjugated dienes,[1-4] we have found long-range contributions of the *gem*-dimethyl group to the chemical shifts of the carbon atoms belonging to the chain. These effects are evident only when long sequences of I are present, and they disappear when the chain segment joined to the *gem*-dimethyl group does not contain other groups of the same type. If we consider, for instance, the segment of chain labeled A, the effects of the *gem*-dimethyl group



$$-CH_2-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\underset{\beta}{CH_2}-\underset{\gamma}{CH_2}-\underset{\delta}{CH_2}-\underset{\epsilon}{CH_2}-\underset{\zeta}{CH_2}-$$

A

are evident, in the spectra obtained at 25.14 MHz, only up to the methylene in the δ position while they are negligible on the ϵ and ζ carbons.[4] Conversely, large effects are observed for the carbon in the ζ position when the chain segment contains other *gem*-dimethyl groups,[3] as in B. These long-range effects allow us to distinguish pentad



$$-CH_2-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\underset{\beta}{CH_2}-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\underset{\delta}{CH_2}-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\underset{\zeta}{CH_2}-$$

B

signals in the copolymer spectra for the quaternary carbon and methyls as well as hexad signals for the methylene of I.

A 50.3-MHz instrument allows further resolution of the peaks, and heptad signals of the quaternary carbon and methyls and octad signals of methylene become evident. Figure 1 shows some regions of the ^{13}C NMR spectrum of a hydrogenated isobutylene-*trans*-1,3-pentadiene (P) copolymer containing 32 mol % of P. Figure 1A illustrates the resonance of the CH_2 group of I in the homopolymeric tetrad. This signal appears as a triplet in the spectrum recorded at 25.14 MHz, corresponding to the hexads IIIIII, PIIIII + IIIIIP, and PIIIIP, i.e., to the four hexads having at the extremities two I units, one I and one P unit, and two P units.[3] A further separation of the peaks appears at 50.3 MHz, as Figure 1A shows. The peak of the homopolymeric hexad is not split, as expected, into three peaks

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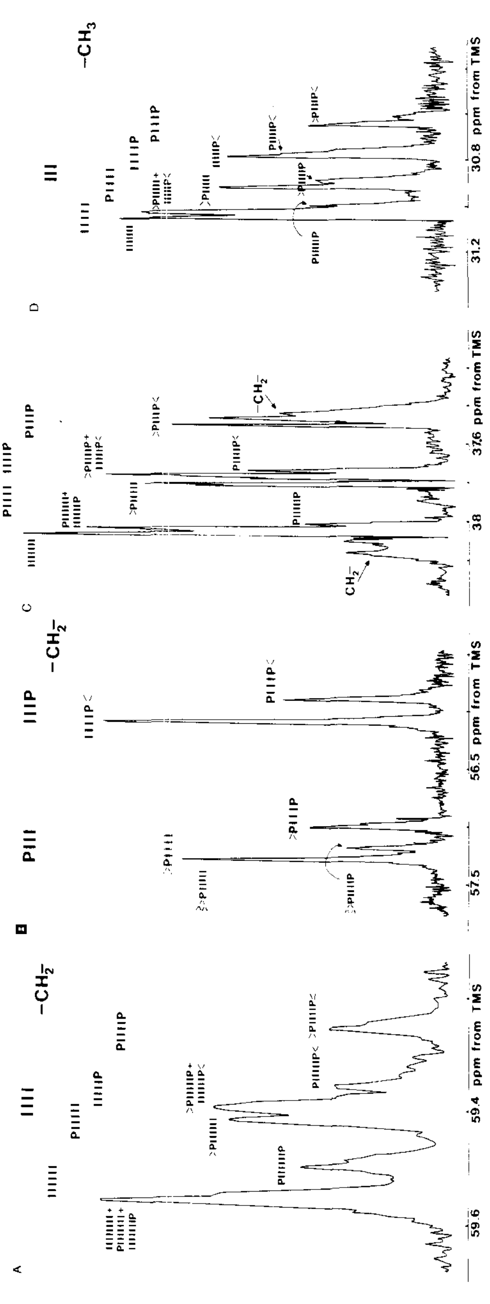


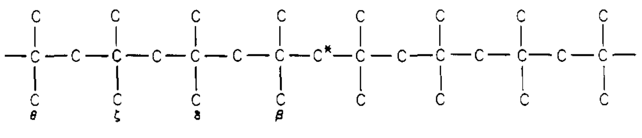
Figure 1. (A) Octad signals of the CH_2 group of I in the homopolymeric tetrad IIII. (B) Octad signals of the CH_2 group of I in the tetrads IIIP and PIII. (C) Heptad signals of the quaternary carbon. (D) Heptad signals of the methyl carbons of the *gem*-dimethyl group.

by the octads having two I units, one I and one P unit, and two P units at the extremities. That occurs because the signals of the octads IIIIIIII and PIIIIIII + IIIIIIIP overlap, as revealed by intensity measurements of the signals. However, the signal of octad PIIIIIIP is separate from the other peaks. The resonances of the hexads PIIIII and IIIIIP appear at 50.3 MHz as distinct signals, whereas at 25.14 MHz the peaks overlap.[3] Since the former hexad contains a methyl in the ζ position which is absent in the latter hexad, the downfield resonance is assigned to the PIIIII hexad and the upfield one to the IIIIIP hexad. Both hexad signals are in turn split into two signals corresponding to the octads >PIIIIII and >PIIIIIP (centered on the first hexad) and IIIIIIP< and PIIIIIP< (centered on the second hexad).[5] Owing to the overlapping of the two resonances shown in Figure 1A, the fine structure of the signal appears as a triplet. The signal upfield is assigned to the hexad PIIIIP and, as expected, does not show fine structure because the effects of the lateral units situated beyond the diene units are lacking. Conversely, fine structure is present in the >PIIII hexad signals (Figure 1B).

A doublet results from the $(>)_2$PIIIII and $(>)_2$PIIIIP octads. Contrary to expectation, no fine structure is observed for the signal of the IIIIP< hexad, which appears as a singlet having, obviously, an intensity which is equal to the sum of the intensity of the peaks due to the >PIIII hexad. It is worth noting that this lack of resolution is accompanied by a minor separation of the doublet due to the PIII tetrad relative to the doublet of the IIIP tetrad.

Fine structure is also present in the regions of the spectrum pertaining to the quaternary carbon and the methyls of I. Figure 1C,D shows the resonances due to the homopolymeric triads of the two mentioned carbon atoms. At 25.14 MHz pentad signals are observed. When the spectrum is recorded at 50.3 MHz, further separation results and heptad signals arise. The region of the quaternary carbon is slightly complicated by the presence of the two signals, due to a methylene, as reported in previous work. Therefore, the spectra obtained at 50.3 MHz allow us to find long-range effects of the *gem*-dimethyl group.[3]

The findings reported above allow us also to conclude, by applying the additivity scheme, that a θ effect is present on the methylene marked with the asterisk of the chain segment labeled C. In reality, these long-range effects



C

cannot be considered true additive contributions because they are present only in chain segments crowded by methyls, as it occurs in the polyisobutylene chain, whereas they become negligible in other cases. However, the additive character of these effects is noteworthy. Their values are usually positive and they decrease when the distance increases. Therefore, it may be useful to maintain the scheme of the additivity rules during the assignment approach even though these long-range contributions arise, in reality, from conformational effects.

^{13}C NMR spectra were obtained with a Varian XL-200 instrument, working at 50.3 MHz, and using copolymer solutions in 1,2,4-trichlorobenzene at 120 °C.

For resolution enhancement a combination of exponential, Gaussian, and convolution-difference weighting was used. Exponential time constants were in the range of +0.25 to +0.4 s.

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(5) The notation >P signifies PP or IP. Analogously the notation $(>)_2$P means IIP or PIP or IPP or PPP.

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Formation Mechanism of Kink Bands in Modification II of Poly(vinylidene fluoride). Evidence for Flip-Flop Motion between TGTḠ and TḠTG Conformations[1]

In a previous paper,[2] it was reported that the X-ray diffuse streak scatterings found on the fiber diagram of modification II (Figure 1), which was prepared by heat treatment with the ends fixed, are attributed to kink bands *contained in the crystallite. In the kink bands,* the molecule assumes a planar zigzag conformation, and, therefore, a molecular chain consists of both regular TGTḠ and planar zigzag segments in the crystallite. The intensity distribution calculation was carried out for the X-ray diffuse streak scatterings. This suggested that the kink bands are one monomeric unit thick and are mainly formed by the flip-flop motion between TGTḠ and TḠTG conformations during the heat treatment of a fiber specimen of modification II. We briefly describe here results of the intensity distribution calculation.

When the kink bands are formed in a crystallite of modification II, the molecular conformation changes that occur depend upon whether *the number of monomeric* units constituting the kink in a molecular chain is odd or even:

odd $\cdots\mathrm{TGT\bar{G}TGT\bar{G}TGT\bar{G}\underline{T}GT\bar{G}}\cdots \rightarrow$
$\cdots\mathrm{TGT\bar{G}\underline{TT}TGT\bar{G}TGT\bar{G}TG}\cdots$

even $\cdots\mathrm{TGT\bar{G}TGT\bar{G}TGT\bar{G}\underline{T}GT\bar{G}}\cdots \rightarrow$
$\cdots\mathrm{TGT\bar{G}\underline{TTTT}TGT\bar{G}TGT\bar{G}}\cdots$

(underline denotes the kink)

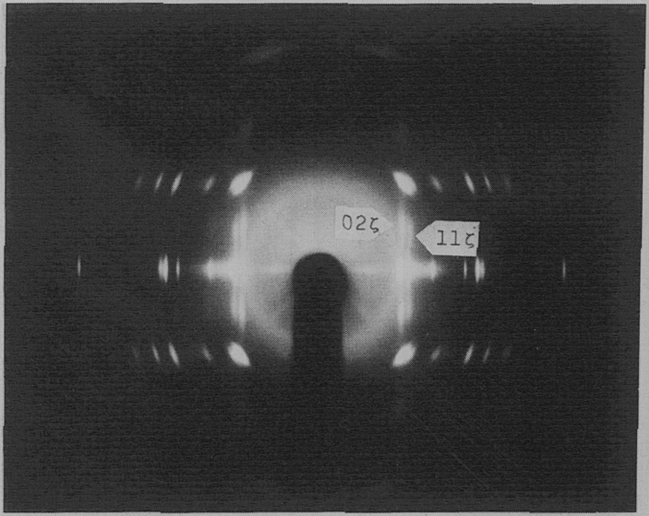

Figure 1. Fiber diagram of modification II giving the X-ray diffuse streak scatterings.

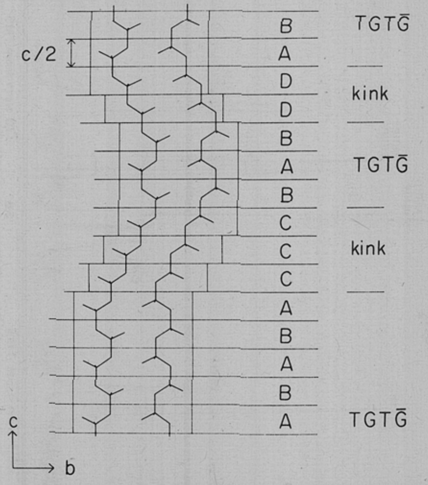

Figure 2. Construction of modification II containing the kink bands (model I) with four kinds of unit-layer structures.

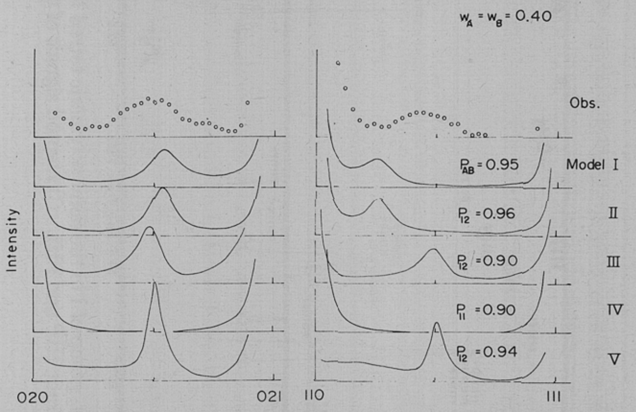

Figure 3. Observed and calculated intensity distributions along the X-ray diffuse streak scatterings on 02ζ and 11ζ.

When the kink is composed of an odd number of monomeric units, the conformation after the kink must change from TGTḠ to TḠTG. If it does not, the chain direction of the regular TGTḠ segment makes an angle with the fiber direction. This contradicts the X-ray diffuse streak scatterings which require the chain direction of the regular segment to be parallel to the fiber direction.[2] When the kink has an even number of monomeric units, the regular segments retain their TGTḠ conformation during the formation of the kink bands. Accordingly, the kink is formed only by the conformational change from G or Ḡ to T which forms the kink itself. By taking the above-mentioned facts into account, we built five kink-band models (models I–V) and calculated the intensity distributions along the X-ray diffuse streak scatterings by using the intensity equation for stacking faults.[3-5] Here, for the case of a kink with an odd number of monomeric units, only the kink with one monomeric unit was considered because it is unlikely that kinks with an odd number of monomeric units equal to or more than three are exclusively formed without the formation of kinks with an even number of monomeric units. For example, a kink with three monomeric units can be formed by a conformational change from G or Ḡ to T in three subsequent monomeric units and from TGTḠ to TḠTG in the regular segment. Energetically, the kink with two monomeric units, which is formed only by the conformational change from G or Ḡ to T in two subsequent monomeric units, is considered *to be formed more easily than a kink with three monomeric* units.

The structure of modification II containing the kink

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