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Isomorphism Phenomena in Isotactic Poly(4-methyl-substituted α-olefins) and in Isotactic Poly(alkyl vinyl ethers)

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ABSTRACT: The systems 4-methyl-1-pentene/4-methyl-1-hexene and isopropyl vinyl ether/*sec*-butyl vinyl ether have been studied as copolymers and as homopolymer mechanical mixtures. For both systems, in either case, isomorphism phenomena have been seen on the basis of X-ray diffraction. While the chain axes and the chain symmetries are the same as those of pure homopolymers, the equatorial dimensions of the unit cells are a regular function of composition. The melting points of the copolymers are a function of composition and are always between the melting temperatures of the pure homopolymers. No isomorphism phenomena have been seen in the homopolymer mixtures poly(4-methyl-1-pentene)/poly(isopropyl vinyl ether) and poly(4-methyl-1-hexene)/poly(*sec*-butyl vinyl ether).

Isomorphism phenomena in the macromolecular field have been recognized by many authors.[2–5] Here we recall that they may be distinguished into two different classes: (a) chain isomorphism, where chemically and structurally different macromolecules are present in the same crystalline phase, and (b) isomorphism among different monomeric units, which occurs in the crystalline copolymers containing a more or less random distribution of comonomer units. It is also well known that isomorphism requires that the two types of macromolecules or of monomeric units be similar in the solid state both in conformation and in size. Bearing in mind these conditions, we prepared first binary mixtures of isotactic poly(4-methyl-1-pentene) (PMP) with isotactic poly(4-methyl-1-hexene) (PMHE), and of isotactic poly(isopropyl vinyl ether) (PIPVE) with isotactic poly(*sec*-butyl vinyl ether) (PSBVE). Successively, we prepared a series of copolymers of 4-methyl-1-pentene (MP) with 4-methyl-1-hexene (MHE) and of isopropyl vinyl ether (IPVE) with *sec*-butyl vinyl ether (SBVE).

In the following we will refer to the preparation of the binary mixtures and of the copolymers obtained. Then we will demonstrate the existence of isomorphism in all these cases on the basis of X-ray evidence and for the copolymers also on the basis of the melting point *vs.* composition curves.

Experimental Section

A. Polymers and Copolymers Preparation. 1. 4-Methyl-1-pentene and 4-Methyl-1-hexene System. Racemic and optically active (optical purity 93%) 4-methyl-1-hexene[6] and the Fluka A. G. "purum" 4-methyl-1-pentene, both defined pure by gas chromatographic analysis, were polymerized with Ziegler–Natta catalysts. The catalysts were obtained by allowing either technical $TiCl_4$ or "ARA" $TiCl_3$ to react with freshly distilled $Al(i\text{-}C_4H_9)_3$ or $Zn(i\text{-}C_4H_9)_2$ prepared from $Al(i\text{-}C_4H_9)_3$ and $ZnCl_2$.

The catalyst was prepared at 0°, in a glass cylinder, under dry nitrogen atmosphere and in the presence of an aliphatic hydrocarbon, either by adding the organometallic compound to "ARA" $TiCl_3$ or by adding $TiCl_4$ to the organometallic compounds.

After the monomer addition, the glass cylinders were sealed and occasionally shaken at room temperature for several days. Polymerization was stopped by adding methanol and the recovered insoluble polymer was purified with methanol-containing HCl and extracted with boiling solvents.[7]

The polymerization conditions are reported in Table I.

2. Isopropyl Vinyl Ether and Racemic *sec*-Butyl Vinyl Ether System. The homopolymers of racemic *sec*-butyl vinyl ether and of isopropyl vinyl ether, as well as the copolymers of the two monomers considered, were prepared by polymerization of the corresponding monomers or mixtures of the two monomers, in glass flasks, equipped with side openings for the introduction of the reagents and of nitrogen. The catalyst system used was based on $Al(O\text{-}i\text{-}C_3H_7)_3$–anhydrous H_2SO_4 and $Al(i\text{-}C_4H_9)_3$–THF as an activator.[8,9]

The catalyst was prepared as previously[9] described by adding, under nitrogen atmosphere, anhydrous H_2SO_4 (0.77

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TABLE I
HOMO- AND COPOLYMERIZATION OF 4-METHYL-1-HEXENE (I) AND 4-METHYL-1-PENTENE (II)

	Monomer					
Run	I	Mol	II, mol	Solvent (ml)	Catalyst[a]	Monomer[b]/$TiCl_n$
A	(*R*)(*S*)-4-Methyl-1-hexene	0.135		Isocatane (55)	$TiCl_3$"ARA"/$Al(i\text{-}C_4H_9)_3$	33
B			0.119	*n*-Octane (20)	$TiCl_4/Al(i\text{-}C_4H_9)_3$	50
C	(*R*)(*S*)-4-Methyl-1-hexene	0.0548	0.0548	*n*-Heptane (15)	$TiCl_4/Zn(i\text{-}C_4H_9)_2$	30
D	(*S*)-4-Methyl-1-hexene	0.0276	0.0274	*n*-Octane (15)	$TiCl_4/Zn(i\text{-}C_4H_9)_2$	30
E	(*S*)-4-Methyl-1-hexene	0.0143	0.0429	*n*-Octane (15)	$TiCl_4/Zn(i\text{-}C_4H_9)_2$	30

[a] Molar ratio Me/Ti = 2.5. [b] In moles; in the case of copolymers, the sum of the moles of the two comonomers was considered.

TABLE II
HOMO- AND COPOLYMERIZATION OF RACEMIC *sec*-BUTYL VINYL ETHER (III) AND OF ISOPROPYL VINYL ETHER (IV) BY THE CATALYST SYSTEM $Al(O\text{-}i\text{-}C_3H_7)_3\text{-}H_2SO_4$[a] USING $Al(i\text{-}C_4H_9)_3$-THF[b] AS AN ACTIVATOR

	Monomer, mol							
Run	III	IV	Ethyl acetate, ml	Monomer (III + IV)/H_2SO_4	Monomer (III + IV)/$Al(i\text{-}C_4H_9)_3$-THF	Polymerizn time, hr	Conversion[c]	[η], dl/g
F	0.313		170	100	16	24	41.1	5.5[d]
G		0.100	55	197	15	14	48.4	12.0[e]
H	0.075	0.025	55	197	15	14	35.5	3.5[d]
I	0.050	0.050	55	197	15	14	59.8	6.0[d]
K	0.025	0.075	55	197	15	14	66.7	7.4[e]

[a] Molar ratio $Al(O\text{-}i\text{-}C_3H_7)_3/H_2SO_4$ = 6.83. [b] Molar ratio $Al(i\text{-}C_4H_9)_3$/tetrahydrofuran = 1. [c] Calculated on the basis o the methanol-insoluble polymer. [d] At 30° in toluene. [e] At 75° in toluene.

TABLE III
HOMOPOLYMERS AND COPOLYMERS OF 4-METHYL-1-HEXENE (I) AND 4-METHYL-1-PENTENE (II)[a]

Homopolymers mixtures (I + II)[b]		Copolymers (I + II)		
Sample	II (% by weight)	Sample	II (% by weight)	[η], dl/g[e]
1	10.0	6[c]	52.2	1.05
2	24.7	7[c]	74.2	0.51
3	51	8[d]	50	0.82
4	77.1			
5	90.2			

[a] Benzene extractable and diethyl ether nonextractable fractions were used. [b] I (see run A, Table I) had [η] = 3.95 in tetraline at 120°; II (see run B Table I). [c] In this case comonomer I corresponds to (*S*)-4-methyl-1-hexene (see runs C and E, Table I). [d] In this case comonomer I corresponds to (*R*)(*S*)-4-methyl-1-hexene (see run C, Table I). [e] In tetraline at 120°, using a Desreux-Bischoff dilution viscometer.

TABLE IV
HOMOPOLYMERS MIXTURES AND COPOLYMERS OF RACEMIC *sec*-BUTYL VINYL ETHER[a] (III) AND ISOPROPYL VINYL ETHER (IV)

Homopolymers mixtures[a] (III + IV)		Copolymer[a]	
Sample[b]	Moles of monomeric units deriving from III, %	Sample[b]	Moles of monomeric units deriving from III, %
9	70.6	12	61.5
10	44.8	13	32.0
11	22.3	14	5.0

[a] Prepared using the catalyst system $Al(O\text{-}i\text{-}C_3H_7)_3\text{-}H_2SO_4/Al(i\text{-}C_4H_9)_3$-THF. [b] Nonextractable fraction with boiling ethyl ether, but extractable with boiling benzene in Kumagawa extractor.

ml) to a solution of $Al(O\text{-}i\text{-}C_3H_7)_3$ (19.7 g) in isoctane (28.5 ml); molar ratio $Al(O\text{-}i\text{-}C_3H_7)_3/H_2SO_4$ = 6.83.

The catalyst was added to the solution of the monomer or of the monomers mixture in ethyl acetate at the temperature of 0° under magnetic stirring.

The polymerization was stopped, after maintaining it 2 hr at 0° and 12 or 22 hr at room temperature, by addition of a dilute aqueous solution of ammonia in methanol. The methanol-insoluble polymer was fractionated by boiling solvents. Table II reports the polymerization conditions.

B. Blending of the Polymers. The blends were prepared by slow evaporation of carbon tetrachloride solutions of the poly(α-olefins) or benzene solutions of poly(alkyl vinyl ethers); homogeneous sheets (1-2 mm thickness) were thus obtained. Compositions and properties of the blends obtained are reported in Tables III and IV.

The homopolymers employed to prepare the blends were benzene extractable and diethyl ether nonextractable fractions having high stereoregularity. In the case of poly(α-olefins) care was taken in order to prevent precipitation of the less soluble polymer (PMP) during solvent evaporation. To this purpose, thin solution layers were subsequently evaporated on the same film.

C. Copolymer Samples. The samples were prepared by the same procedure as that described for the preparation of the homopolymers, from the stereoregular fractions of the copolymers, extracted with the same solvents as the homopolymers.

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TABLE V

Polymer	$a = b$, Å	Periodicity per monomer unit along c, Å	M/N monomeric units per pitch	Torsional angles along the main chain	Valence angles along the main chain, deg	Transverse area per molecule, Å^2
Poly(4-methyl-1-pentene)	18.6 ± 0.2	1.97 ± 0.05	3.50 (7/2)	$\sigma_1 = 287°7'$ $\sigma_2 = 167°26'$	$\varphi_1 = 110$ $\varphi_2 = 113$	86.49
Poly(4-methyl-1-hexene)	19.6 ± 0.2	2.00 ± 0.05	3.50 (7/2)	$\sigma_1 = 286°71'$ $\sigma_2 = 169°17'$	$\varphi_1 = 110$ $\varphi_2 = 113$	96.43

The monomeric unit content derived from the comonomers was determined by ir analysis, using a Perkin-Elmer 221 spectrophotometer. Measurements were carried out on nonoriented polymer films.

In the case of α-olefin copolymers,[10] use was made of the absorption bands at 964 and 918 cm^{-1}, characteristic of the monomeric units derived from MHE and MP, respectively. Log ($D_{\text{B}-918\ \text{cm}^{-1}}/D_{\text{B}-964\ \text{cm}^{-1}}$) was determined and compared with the value obtained from mixtures of the two homopolymers with known composition (base line points, 1215 and 895 cm^{-1}).

For the alkyl vinyl ether copolymers[11] the absorption bands at 816 and 852 cm^{-1}, characteristic of the monomeric units derived from SBVE and IPVE, respectively, were used, with base line points 1230 and 770 cm^{-1}.

The melting temperatures were determined by a Perkin-Elmer differential scanning calorimeter; the ends of the fusion peaks have been assumed as melting points (heating rate, 8°/min).

D. X-Ray Analysis of the Homopolymer Mixtures and of the Copolymers. The specimens used in the X-ray analysis generally consisted of thin fibers obtained by stretching, at room temperature, narrow ribbons cut out from the films of the polymers. The X-ray spectra were performed in cylindrical cameras (28.65 mm = R and 57.30 mm = R_1); both Cu Kα and Fe Kα radiations were employed.

Results

4-Methyl-1-hexene and 4-Methyl-1-pentene System. The crystal structures of both isotactic P4MP[12-16] and of isotactic PMHE[12,13,16] have been described as resulting from a tetragonal packing of molecules having a 7/2 helix conformation. Each right-handed helix is surrounded by four left-handed helices and *vice versa*, according to the $P\bar{4}$ space group. The unit cell parameters and the chain conformations of the two polymers are reported in Table V.

The similarity in both chain conformation and cross-sectional area per macromolecule seemed to be favorable prerequisites for cocrystallization. We first examined the binary mixtures of isotactic PMHE and of isotactic PMP. From the position of the X-ray spots, the equatorial unit cell dimensions are seen to change progressively with composition while the c axis retains the value found in the pure homopolymers. The a axis assumes values linearly intermediate between those of the pure homopolymers, the $P\bar{4}$ symmetry being preserved, in the ranges of composition 0–25 and 75–100% of PMP (by weight). In the 25–75% range, a splitting of the spots is observed, corresponding to the separation of the system in two limiting phases having a PMP content of 25 and 75% by weight, respectively.

From the above, we have concluded that the PMP/PMHE system at room temperature represents an example of isodimorphism with a gap of mixing in the 25–75% range of compositions by weight. The melting points of the blendings in the range 1–25% and 75–99%, respectively, of PMP could not be determined possibly for separation of the two components at high temperature. The variation of the a cell parameter with composition is shown in Figure 1. The cocrystallization between the macromolecules of isotactic PMP and the macromolecules of isotactic PMHE is clearly demonstrated.

The X-ray fiber spectra of the copolymers with different contents of 4-methyl-1-pentene and of 4-methyl-1-hexene have shown that both the chain conformation and the unit cell symmetry of the pure homopolymers are maintained in the crystal state. Also in this case, the equatorial unit cell dimensions change progressively with composition and assume values that are intermediate between those of the two pure homopolymers. Contrary to what occurs in the case of the homopolymer binary mixtures, in the case of the copolymers isomorphism exists between the two monomeric units, in the full range of compositions (Figure 2).

The melting points of these copolymers change linearly with composition and are always comprised between those of pure PMP and PMHE (Figure 3A).

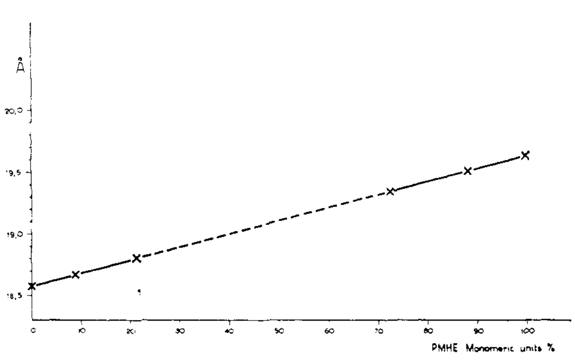

Figure 1. Variation of the a axis of the unit cell with composition in the poly(4-methyl-1-pentene)/poly(4-methyl-1-hexene) mixtures.

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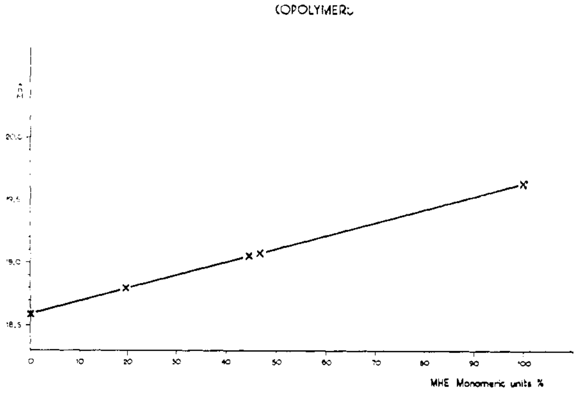

Figure 2. Variation of the *a* axis of the unit cell with composition in the 4-methyl-1-hexene/4-methyl-1-pentene copolymers.

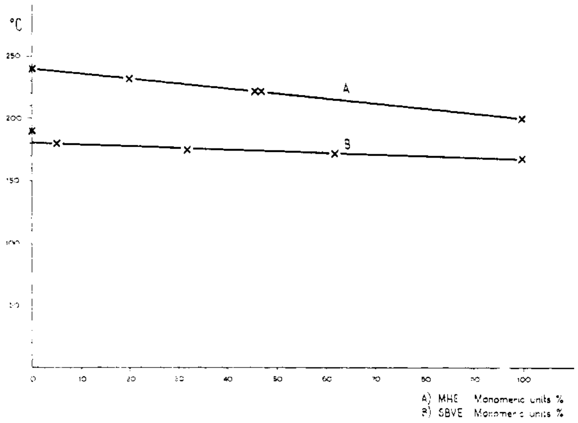

Figure 3. Melting temperatures *vs.* compositions of 4-methyl-1-hexene/4-methyl-1-pentene copolymers (A) and of isopropyl vinyl ether/*sec*-butyl vinyl ether copolymers (B).

Isopropyl Vinyl Ether and Racemic *sec*-Butyl Vinyl Ether System. The crystal structures of isotactic PIPVE[17] and PSBVE[18] were described as resulting from a tetragonal packing of chains having a 17/5 helix conformation. Each right-handed helix is surrounded by four left-handed helices and *vice versa.* In Table VI the unit cell parameters and the parameters of the two helices are reported. The cross-sectional areas per macromolecules in the crystalline state do not differ by more than 11% and the chain conformations are identical.

Table VI

Polymer	$a = b$, Å	Periodicity per monomeric unit along c, Å	M/N monomeric units per pitch	Torsional angles along the main chain, deg	Valence angles along the main chain	Transverse area per molecule, Å^2
Poly(isopropyl vinyl ether)	17.2 ± 0.2	2.09 ± 0.05	3.40 (17/5)	$\sigma_1 = 290$ $\sigma_2 = 170$	$\varphi_1 = \varphi_2 = 114°30'$	73.96
Poly(*sec*-butyl vinyl ether)	18.25 ± 0.2	2.09 ± 0.05	3.40 (17/5)	$\sigma_1 = 290$ $\sigma_2 = 170$	$\varphi_1 = \varphi_2 = 114°30'$	83.27

We first examined the X-ray fiber spectra of the homopolymer mixtures of isotactic PIPVE and PSBVE. From the spots of fiber spectra it is clear that while the unit cell symmetry and the *c* axes of the various mixtures do not change, the *a* axes dimensions continuously change with composition. The continuous change of the *a* cell parameter with composition indicates the existence of a phenomenon of chain isomorphism occurring in the whole range of compositions. In Figure 4 the *a* axes of the two pure homopolymers are compared with those of the crystalline mixtures; within experimental error the *a* length varies linearly with composition.

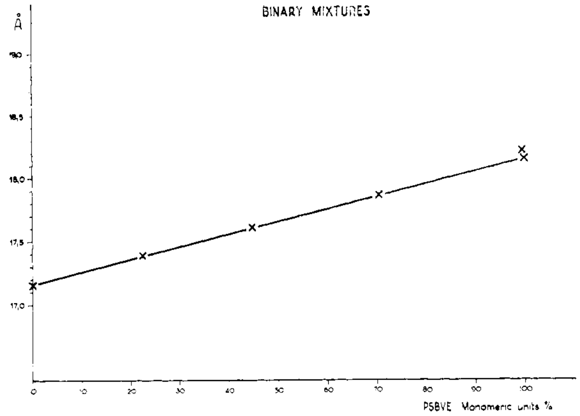

Figure 4. Variation of the *a* axis of the unit cell with composition in the poly(isopropyl vinyl ether)/poly(*sec*-butyl vinyl ether) mixtures.

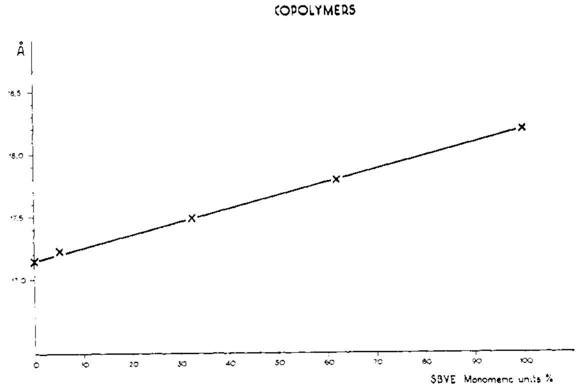

Figure 5. Variation of the *a* axis of the unit cell with composition in the isopropyl vinyl ether/*sec*-butyl vinyl ether copolymers.

The examination of the X-ray fiber spectra of the isopropyl vinyl ether–*sec*-butyl vinyl ether copolymers shows that also in this case, an isomorphism phenomenon occurs between the two monomeric units. Pre-

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serving the *c* axes dimensions and the unit cell symmetry the *a* axes dimensions change almost linearly with composition (see Figure 5) and are always comprised between the values corresponding to the two pure homopolymers.

The melting points of these copolymers are a function of composition and are always between the melting points of the two pure homopolymers (Figure 3B).

As in the preceding system, the behavior of the melting points of the homopolymer mixtures of isotactic PIPVE and of isotactic PSBVE is less clear, possibly owing to separation processes that occur at high temperatures.

Binary Mixtures Containing PMP and PIPVE, and PMHE and PSBVE. The chain conformations and the chain packings of the two poly(α-olefins) are very similar to the chain conformations and chain packings of the corresponding poly(alkyl vinyl ethers). The cross-sectional area in the crystalline state differs by about 12% in both systems. Starting these considerations, it seemed possible that also in these two systems the formation of solid solutions might take place. However, the trials we have conducted have shown that poly(α-olefins) and the corresponding poly(alkyl vinyl ethers) crystallize in separate unit cells in the full range of compositions. This fact may be tentatively attributed to the difference in polarity between the two classes of polymers.

Conclusions

The polymer system consisting of homo- and copolymers of 4-methyl-1-pentene and 4-methyl-1-hexene as well as that derived from isopropyl vinyl ether and *sec*-butyl vinyl ether represent interesting examples of the possible phenomena of isomorphous replacement, in macromolecular systems. Both copolymeric systems show isomorphism in the whole range of compositions. In the case of the homopolymer mixtures, the poly(alkyl vinyl ethers) show the same behavior, whereas the poly(α-olefins) yield isodimorphism, the limiting phases corresponding to about 25% of weight concentration of either component.

It is interesting to observe that only two cases of isomorphism among homopolymers had been previously described: polystyrene and styrene-*p*-methylstyrene copolymer (molar fraction 30% of *p*-methylstyrene[2,3]), poly(vinyl fluoride) and poly(vinylidene fluoride) system.[19] In these cases, in addition to the requisites of size and conformational analogy among the replacing units there is the additional feature of the chemical compatibility among the homopolymer chains. It seems that the last feature is also very important as in the systems consisting of poly(4-methyl-1-pentene) with poly(isopropyl vinyl ether) and of poly(4-methyl-1-hexene) with poly(*sec*-butyl vinyl ether) where, in spite of the over-all size of the chain conformation of the two types of macromolecules being very similar, no isomorphism phenomena have been observed.

Acknowledgment. The A. thank Dr. G. Gianotti for the melting point determinations.

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Configurational Statistics and Stereochemical Structure of Vinyl Polymers

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ABSTRACT: General methods are presented for the calculation of the average conformations of adjoining pairs of bonds in vinyl chains (—CH$_2$—CHR—)$_x$ of any specified stereochemical configuration. Intramolecular interactions are characterized by a small set of statistical weight parameters, usually three in number. Those involving two groups (CH$_2$, CH, and/or R) separated by four bonds are dominant in discriminating between various possible conformations of the chain molecule. Numerical calculations are carried out to illustrate the role of the several kinds of interactions in stereoregular isotactic and syndiotactic chains. The average conformations of one, two, and three consecutive racemic dyads within an otherwise *meso* (isotactic) chain illustrate the effects of the stereochemical configurations of adjoining units. The average conformation of one racemic dyad, or of a pair of racemic dyads, in an atactic chain is subject to wide variation, depending on the stereochemical configurations of sequences of dyads adjoining the one(s) in question. This is demonstrated by generating sets of 100 Monte Carlo chains in which the average incidence of racemic dyads is specified but the sequence in which they occur is random, then carrying out calculations for racemic dyads situated in the chains thus generated. The steric interactions which severely limit the conformations of vinyl chains cause the conformation of a given skeletal bond to be strongly influenced by the conformations of adjoining dyads. This neighbor interdependence renders the average conformation of a given dyad dependent upon the stereochemical configurations of other dyads in the chain, including those removed some distance in the chain sequence.

The conformations accessible to a vinyl polymer chain depend in marked degree on the character of

$$\mathrm{H{-}(CH_2{-}CHR{-})_{\it x}CH_3}$$

the substituent R and on the configurations of the asymmetric centers CHR. If R is a group commensurate in size with or larger than methyl, the number of significant conformations for the chain as a whole is severely restricted by steric interactions between nonbonded atoms and groups. Those conformations which are