Table I
Dihedral Angles (Deg) H_0-C-C-H_k[a] in Five-State Models of Polypropylene and RIS Populations Computed at 140 °C for Infinite Isotactic and Syndiotactic Chains

	dihedral angles				populations			
	model I		model II		model A[c]		model B[d]	
state[b]	$-\phi_1$	ϕ_2	$-\phi_1$	ϕ_2	isotactic	syndiotactic	isotactic	syndiotactic
t	180	65	173	72	0.4502	0.6121	0.4469	0.6034
t*	145	100	138	107	0.0825	0.0435	0.1369	0.0643
g*	100	145	107	138	0.0525	0.0439	0.0277	0.0533
g	65	180	72	173	0.3733	0.2669	0.3532	0.2514
$\bar{g}$	−56	−56	−56	−56	0.0415	0.0336	0.0353	0.0276

[a] Positive clockwise rotations, with $\phi_k = 0°$ for the cis conformation, referred to Figure 1. [b] Defined for the main-chain carbon atoms, using Suter and Flory's notation.[10] [c] Reference 5. [d] Following ref 10.

Table II
Observed and Calculated Vicinal Proton Coupling Constants[a] in Isotactic and Syndiotactic Polypropylene

		isotactic		syndiotactic	
	model	J_{01}	J_{02}	J_{01}	J_{02}
calculated according to Haasnoot et al. (eq 8 of ref 11, parameter set C)	I-A	7.44	6.47	8.80	5.41
	I-B	7.76	6.06	8.82	5.28
	II-A	6.99	6.03	8.44	4.85
	II-B	7.24	5.69	8.46	4.74
calculated with Karplus equation (parameter set III of ref 12)	II-A	6.77	5.92	8.05	4.91
	II-B	6.98	5.60	8.05	4.79
	ref 1	6.7	5.9	7.6	5.2
observed		7.0	5.7	8.3	4.8

[a] Calculated values at 140 °C. Observed values[3] at 150 °C for the isotactic polymer and at 130 °C for the syndiotactic polymer.

chain, while in the case of the isotactic polymer the former model underestimates the difference $J_{01} - J_{02}$ and the latter one overestimates it. The different behavior originates mainly from the population of the dyad state tt* (in Suter and Flory's notation), which in model B is about twice as large as in A.

(iv) The Karplus equation derived from the analysis of 1,3,5,7-tetramethylcyclooctanes[12] yields results quite similar to the equation of Haasnoot et al.[11] Model II-B seems somewhat superior to II-A when this Karplus equation is used.

(v) Both models II-A and II-B reproduce the four values of J_{0k} with equal or better accuracy than the method of Brückner et al.[1] In light of the present results, the conclusions reached by these authors concerning the relative populations of the less stable states seem questionable. For example, according to Brückner et al., in the isotactic chain the easiest helix inversion (in the sense which involves a syn–axial interaction) occurs via the conformational sequence /tg/g*t/gt/. In both models A and B the /g*t/ state is unfavored by an extra gauche interaction, as was indicated by the results of energy calculations[9,10] based on interactions between all atoms (i.e., including all the hydrogen atoms). This suggests that the stabilization of the /g*t/ state in the calculations of Brückner et al.[1] may be an artifact arising from considering the methyl groups and the terminal CH_x groups of a dyad as spherical pseudoatoms. According to model B the inversion occurs mainly through states /tt*/, while according to A inversions via distorted /tg/gt/ states are about as probable as via /tt*/. At present it appears that different models can allow approximately the same flexibility to the chain, but the balance between different states is still subject to some degree of uncertainty.

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Steric Energy of the Rotational State of the Side Groups of Poly(vinylnaphthalene)

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Poly(1-vinylnaphthalene) (PIVN) and poly(2-vinylnaphthalene) (P2VN) molecules have bulkier side groups than polystyrene (PS) derivatives. The steric conformation of these naphthyl side groups in polymers in solution and dynamic properties of poly(vinylnaphthalene) (PVN) in solution have attracted the interest of investigators in the fields of NMR spectroscopy[1] and fluorescence spectroscopy.[2-4]

Although P2VN and P1VN are isomeric, they exhibit rather different properties in solution; the behavior of the former resembles that of PS. Transitions are observed at about 50–80 °C in P2VN[5] and PS[6] in solution and the ^1H NMR spectral patterns are similar.[1] The differences between P1VN and P2VN are possibly due to differences in their rotational isomeric states (RIS). The phenyl group in PS has a C_{2v} symmetry axis along the plane of the ring and there is no RIS for the side group. Presumably in P1VN, the 1-naphthyl group may be limited to a single conformation, which may be different from those for the 2-naphthyl or phenyl groups.

In order to elucidate the RIS of the pendant groups in P1VN and P2VN, we estimated the steric energy of the

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Table I
Steric Energy of the Pentad Model of P1VN with Terminal Methyl Groups[a]

configuration	RIS of side group/steric energy (kcal mol^{-1})							
syndiotactic (tttt)	$\pi\pi\pi$ 0.00	$\pi\pi o$ 3.19	$\pi o\pi$ 4.35		$o\pi o$ 6.37	$oo\pi$ 7.29		ooo 10.3
isotactic (tgtg)	$\pi\pi\pi$ 0.00	$o\pi\pi$ 0.47	$\pi o\pi$ 1.63	$\pi\pi o$ 1.74	$oo\pi$ 2.07	$o\pi o$ 2.75	πoo 3.46	ooo 4.75
heterotactic (tttg)	$\pi\pi\pi$ 0.00	$\pi\pi o$ 2.00	$\pi o\pi$ 3.07	$o\pi\pi$ 3.28	πoo 4.80	$o\pi o$ 5.18	$oo\pi$ 5.55	ooo 7.34

[a] All values are evaluated relative to the $\pi\pi\pi$ conformer.

Table II
Steric Energy of the Pentad Model of P2VN with Terminal Methyl Groups[a]

configuration	RIS of side group/steric energy (kcal mol^{-1})							
syndiotactic (tttt)	$\pi\pi\pi$ 0.00	$o\pi\pi$ 0.33	$o\pi o$ 0.48		$\pi o\pi$ 0.70	$oo\pi$ 0.82		ooo 0.91
isotactic (tgtg)	$oo\pi$ −0.11	$o\pi\pi$ −0.03	$\pi o\pi$ −0.01	$\pi\pi\pi$ 0.00	ooo 0.03	πoo 0.09	$o\pi o$ 0.09	$\pi\pi o$ 0.15
heterotactic (tttg)	$\pi\pi o$ −0.03	$\pi\pi\pi$ 0.00	$o\pi o$ 0.18	$o\pi\pi$ 0.22	πoo 0.27	$\pi o\pi$ 0.30	ooo 0.33	$oo\pi$ 0.35

[a] All values are evaluated relative to the $\pi\pi\pi$ conformer.

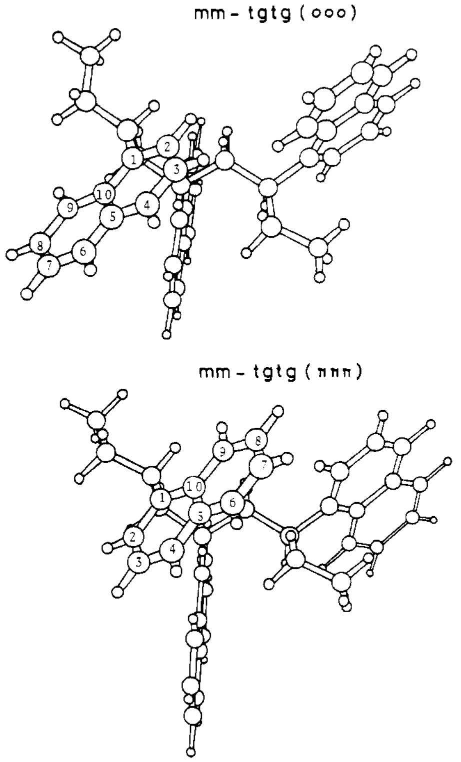

Figure 1. Schematic representation of the rotational isomeric states of the side groups in (mm)-P1VN chain: (top) *o* conformation; (bottom) π conformation. In the P2VN chain, the α carbon is bonded to the C(2) atom in the naphthyl group.

RIS of the naphthyl groups in P1VN and P2VN on the basis of the conformations of the main chains, which are similar to those for other vinyl aromatic polymer chains, using a force field method (FFM).

Method of Calculation

The calculation of the steric energy of P1VN and P2VN having preferred main-chain conformations corresponding to those of the pentad model of PVN with methyl groups at the terminals was performed on an IBM 370/138 computer using Allinger's QCPE FFM program.[7-10] The steric energy of the molecule is written as $E_{\text{steric}} = \sum_{\text{bonds}} E_{\text{bond stretch}} + \sum_{\text{angles}} E_{\text{bend}} + \sum_{\text{torsions}} E_{\text{torsion}} + \sum_{\text{vdW's}} E_{\text{vdW}} + \sum_{\text{str-bnd's}} E_{\text{str-bnd}}$, where the terms, in order, are the stretching energy for each bond, the bending energy for each bond angle, the torsional energy for each skeletal bond, the nonbonded van der Waals energies among all atoms, and the stretch–bend interaction energies. The minimization of the steric energy was achieved by using an improved steepest descent method.

The skeletal chain conformations for PVN were assumed to be those which are generally preferred for vinyl polymers.[11] However, not all the skeletal conformations for vinyl polymers are preferred conformations for PVN (especially for P1VN). Therefore, we examined the conformational stability of PVN using the atomic models. We conclude that for P1VN, the principle preferred conformations are tgtg (gtgt), tttt, and tttg in isotactic, syndiotactic, and heterotactic sequences, respectively. The other skeletal conformations were rejected because of high-energy steric overlaps between the naphthyl group and the neighboring unit.

1-Naphthyl and 2-naphthyl rings have no axis of symmetry and there are therefore two rotational isomeric states relative to the methine proton. Figure 1 shows a schematic representation of the RIS. The RIS of the top and bottom parts of Figure 1 are designated as *o* and π conformations, respectively.

From these considerations, we calculated the steric energy of PVN for the standard conformations which have the preferred skeletal conformations and the various rotation angles of the RIS (0° or 180°) for the side groups and carried out minimization of the steric energy. The dihedral angles about the main-chain bonds and the rotational angles of the side group in the optimized conformations were displaced by ±10° relative to the standard conformation.

Results and Discussion

The calculated steric energies for P1VN and P2VN are given in Tables I and II, respectively. The results are given in kcal/unit relative to the steric energy of each $\pi\pi\pi$ conformer of the side group. For the P1VN chain, the energy difference between the *ooo* and the $\pi\pi\pi$ conformer is large (5–10 kcal/mol). When one of the π conformations is changed to a o conformation, the steric energy of that conformer increases by about 3.8, 1.3, and 2.8 kcal/mol in syndiotactic, isotactic, and heterotactic sequences, respectively. Therefore, for the naphthyl group in P1VN, the π conformation is believed to be more stable than the o conformation.

The origin of the steric energies of the conformers is mainly attributed to the difference in the van der Waals (nonbonded) interaction energy and the bending energy of the bond angles. The optimized distance between the methine hydrogen and the hydrogen of the naphthyl ring in the same monomer unit was obtained as follows: in the o state, the distance from the hydrogen atom bonded to C(2) is 2.27 Å (1.02 kcal/mol), and in the π conformation the distance from the hydrogen atom bonded to C(9) is 2.16 Å (1.89 kcal/mol). If the interaction between the methine and naphthyl group is the only effective interaction within the same monomer unit, the o conformation is more stable than the π conformation. However, the o conformation imposes steric overlap between the hydrogens at C(9) in a rotating naphthyl ring and one of the methylene or α carbons which belongs to the adjacent monomer unit: the hydrogen atom on C(9) takes the center position of the two adjacent methylene hydrogens or the methylene hydrogen and the α-carbon atom in the adjacent monomer unit. In the optimized states, this hydrogen would be located at a position equidistant (2.25 Å) from the two methylene hydrogen atoms on each side. Consequently, the rotational freedom of the naphthyl groups should be strongly restricted in the o conformation. In the π conformation, the energy falls rapidly as the steric repulsions between the naphthyl groups are relieved by an increase in rotation of the side group. In the o conformation, as mentioned above, the energy does not fall as much as in the π conformation by the optimization process. An increase of the bending energy of the bond angle in the o conformation is also ascribed to the intense interaction between H(9) and the adjacent methylene hydrogen atom: the bending interactions of $CH_2{-}\alpha C{-}CH_2$, $C_{aromatic}{-}\alpha C{-}CH_2$ and $H_{methine}{-}\alpha C{-}CH_2$ become important.

For the P2VN chain, the $\pi\pi\pi$ conformer may not always be of lowest energy: the $oo\pi$ conformer for isotactic and the $\pi\pi o$ conformer for heterotactic sequences are the most stable for the P2VN chain. The difference in steric energy between these conformers was about 0.91–0.26 kcal/mol. On the basis of the calculated results for the P2VN chain, which has the preferred conformation in the main chain, there were no appreciable nonbonded and bending interactions between the C(6) to C(9) atoms or the hydrogen atoms bonded to them (Figure 1) and the main chain (or the neighboring side groups). The extent of the interaction between the 2-naphthyl group and the main chain was almost of the same order as that in PS.

In order to estimate the curves of the potential energy as a function of the rotation angle of the aromatic ring for P1VN, P2VN, and PS, we used Tonelli's model.[12] The curves for P1VN did not resemble those for P2VN and PS, as we expected. On the other hand, the curves for P2VN correspond well to that for PS. The above results suggest that there is little conformational difference in the rotational states of P2VN and PS.

The conclusions obtained from Tables I and II are as follows: (a) In the P1VN chain, the π conformation is the preferred conformation. (b) In the P2VN chain, both the π and o conformations are stable conformations, the side-chain rotational state does not have a great influence upon the conformational stability of the main chain, and the circumstances are quite similar to those of PS.

Finally, it may be assumed that the difference of the RIS of the side groups between P1VN and P2VN probably leads to different solution behavior, as, for example, the ^{1}H NMR spectra or transition phenomena.

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Polymerization and Copolymerization of Vinylisoxazole Derivatives

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Introduction

Among polymerizations of vinyl heterocycles reported in the literature, studies involving isoxazole monomers[1] are rather seldom met. Nevertheless, macromolecules with pendant isoxazole residues could show interesting physical and chemical properties owing to the polarity, basicity, and coordinative power of such a ring. Besides, the ring's characteristic reactivity allows it to be transformed, by suitable reagents, into noncyclic 1,3-difunctional systems; i.e., the isoxazole nucleus could be a useful protecting group in the synthesis of polyfunctional polymers.

This paper deals with radical polymerization and copolymerization of 3,5-dimethyl-4-vinylisoxazole (I) and 5-vinylisoxazole (II) with styrene, acrylic acid, and other selected comonomers.

Results

Preparation and purification of reagents are reported in the Experimental Section.

Monomers I and II were homopolymerized and copolymerized with styrene and acrylic acid using azobis(isobutyronitrile) (AIBN) initiation. Other copolymerizations were carried out with comonomers selected on the basis of an approximate Q–e scheme to space out the isoxazole units as much as possible in order to prevent undesired interactions when the polymers are submitted to chemical transformations and to improve solubility in aqueous media at different pH values, keeping in mind that 3-unsubstituted isoxazole derivatives are unstable in the presence of bases. On account of this I was copolymerized with 4-vinylpyridine and 2-vinylpyridine and II was copolymerized with 2-vinylthiophene in the presence

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