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Conformational Characteristics of Poly(vinylnaphthalene)s from Energy Contour Map

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In poly(1-vinylnaphthalene)(P1VN) and poly(2-vinylnaphthalene)(P2VN), conformational energies of meso and racemic dyads were computed as functions of skeletal bond and side group rotations (0°(*o*) or 180°(π)). The calculation was carried out according to the truncation procedure proposed by D.Y.Yoon. The backbones in P1VN and P2VN were limited to just two rotational states, trans (t) and gauche (g) conformation. The steric interactions involving the bulky naphthyl group precluded $\bar{g}$ conformation; a similar situation occurs in polystyrene. Numerical results suggested these conclusions: the excimer forming site conformations for P1VN were meso : tt($\pi\pi$) and racemic : tt($\pi\pi$) states, and for P2VN were meso : tt($\pi\pi$), tt(*oo*), tt(*o*π), and tt(π*o*) states. These conformations could also be correlated to the dual emissions observed in P1VN and P2VN.

In a previous paper,[1)] we pointed out the differences in some solution properties between poly(1-vinylnaphthalene) (P1VN) and poly(2-vinylnaphthalene) (P2VN), and also the resemblance of the latter to polystyrene in solution. We discussed the conformation of pendant groups in P1VN and P2VN. In another paper,[2)] we treated the steric effect on ^{13}C NMR chemical shifts in poly(vinylnaphthalene)s (PVN), taking into account the Rotational Isomeric State (RIS) of the pendant group; this was based on discussions in the preceding paper.[1)] In PVN, the ring current effect by naphthyl groups was rather small and there was not much difference between P1VN and P2VN. The different spectral patterns in ^{13}C NMR spectra of the aliphatic carbon region were attributed to the difference of the degree of the steric compression shift induced by the steric interaction between the methine hydrogen and the atoms in the naphthyl group.

Among recent discussions on the conformation of PVN, one of the most interesting problems is the studies on the excimer fluorescence of PVN in solutions.[3)] Hirayama[4)] proposed the "$n=3$ rule" for the intramolecular excimer formation and indicated that an excimer was an electronically excited molecular complex formed between two aromatic chromophores in a coplanar sandwich arrangement. For a P2VN chain which satisfies the $n=3$ rule, Frank *et al.*[5)] studied the geometrical arrangement of two chromophores in an excimer state in detail: the conformations of the possible excimer forming site were found to be tt for the isotactic and t$\bar{g}$ or $\bar{g}$t for the syndiotactic chain. He concluded that the ground state (preferred conformation) was tg or gt for isotactic chain, and tt for syndiotactic chain. These results have been predicted by a simple statistical model with RIS approximation. However, in the conformational analysis of PVN in terms of rotations around the skeletal bonds, a more attractive procedure is the preparation of conformational maps developed by Flory *et al.*[6)–10)] The detailed discussion should be based on the average energy $\langle E \rangle_s$ for each rotational state s of skeletal bonds derived from the conformational maps. The purpose of this paper is to discuss the RIS for skeletal bonds in P1VN and P2VN chains, which are closely related to the ground site and excimer forming site conformation.

Calculation

Recently, Sundararajan reported the conformational maps in terms of skeletal bond rotations ϕ_i and ϕ_{i+1}, for the meso and the racemic dyads of poly(*N*-vinylcarbazole) (PVCz).[11)] In PVCz chain, the skeletal bond angle θ (at the methylene carbon atom: αC–CH$_2$–αC) in the minimum energy position in the tt state of the meso and the racemic dyads was larger than that in the other conformations. Since PVN chains have bulky side groups like those of the PVCz chain, the energy maps are computed by varying the bond angles θ from 114° to 126° in steps of 2° at each (ϕ_i, ϕ_{i+1}) grid point. RIS of side groups in PVN are also taken into account in conformational maps.

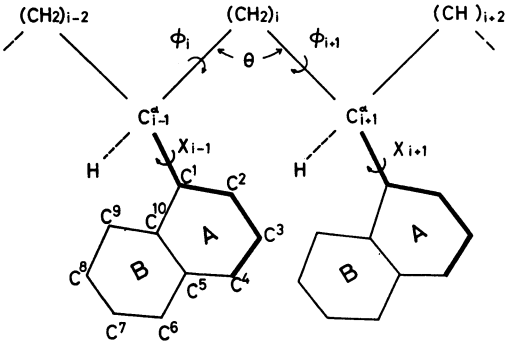

Fig. 1. Portion of the isotactic P1VN chain in the all-trans ($\pi\pi$) conformation. In the P2VN chain, the α-carbon is bonded to the C(2) atom in the naphthyl group.

Table 1. Geometrical parameters

Bond length	l/Å	Bond angle	ϕ/°
C–C	1.53	$\angle$CC$^{\alpha}$–C	112
		$\angle$C$^{\alpha}$–CC$^{\alpha}$	Variable
C$^{\alpha}$–C^{ar}	1.51	$\angle$CC$^{\alpha}$–C^{ar}	112
C–H	1.10	$\angle$CC$^{\alpha}$H	107
C^{ar}–H	1.10	$\angle$C$^{\alpha}$CH=$\angle$HCH	110
C^1–C^2	1.36	$\angle$C^{1}C^{2}C^3	121
C^2–C^3	1.42	$\angle$C^{1}C^{10}C^9	122
C^1–C^{10}	1.43	$\angle$C^{1}C^{10}C^5	119
C^{10}–C^5	1.41	$\angle$C^{2}C^{1}C^{10}	120

Figure 1 shows that the meso : tt state of P1VN chain is occupied by π-conformation. According to the convention of Flory *et al.*,[10] the torsional angles ϕ_i and ϕ_{i+1} for meso *dl* dyads (see Fig. 1) are measured in the right- and left-handed senses, respectively. For the racemic *dd* dyad, ϕ_i and ϕ_{i+1} are measured in the right-handed sense. The bond lengths and bond angles for PVN are given in Table 1.[10] The conformational parameters for naphthyl group were taken from studies on the crystal structure of naphthalene.[12]

In previously calculated results of steric energies for pentamer models,[1] the optimized rotational angles of 1- and 2-naphthyl rings did not exceed $\pm 4.5°$ away from the position where the ring was perpendicular to the plane made by the adjoining backbone bonds. Accordingly, the rotational angles X (see Fig. 1) of the naphthyl groups are fixed at 0° (*o*-conformation) or 180° (π-conformation).

The nonbonded van der Waals energy among all atoms was computed using the Lennard-Jones 6—12 potential function:

$$E_{\mathrm{vdw}} = a_{i,j}/(r_{i,j})^{12} - c_{i,j}/(r_{i,j})^{6}, \quad (1)$$

where radii, polarizabilities and effective numbers of electrons for C_{sp2}, C_{sp3}, and H were taken from Flory *et al.*[10] Torsional energies for ϕ_i and ϕ_{i+1} were calculated using the intrinsic three-fold torsional function:[7]

$$E_{\mathrm{tor}} = (V/2)(1+\cos 3\phi), \quad (2)$$

where ϕ is the dihedral angle and V is a barrier of 2.8 kcal mol^{-1}.† The deformation energy for the bond angle θ was treated in the harmonic approximation:[9]

$$E_{\mathrm{bend}} = (K_\theta/2)(\theta-\theta_0)^2, \quad (3)$$

where θ_0 was assigned as tetrahedral, and K_θ is the bending constant of 0.044 kcal mol^{-1} deg^{-2}.†† Energies used for construction of the contours were computed at intervals of 5° in ϕ_i and ϕ_{i+1}. These functions were appropriate to reproduce the unperturbed dimensions of PVCz and polystyrene.[10,11]

Results and Discussion

The conformational energies for the meso and the racemic dyads of P1VN chain occupied by π-conformation, using $\theta = 114°$, are shown in Figs. 2 and 3 as functions of the skeletal bond rotational angles ϕ_i and ϕ_{i+1}, respectively. Contours are shown at the energies quoted in kcal mol^{-1} relative to the minimum for the meso : tg (10,105°) or gt (105,10°) state. The tt states for the meso and the racemic dyads did not appear in the energy map until θ went beyond 116°. This feature of the energy surface is a consequence of the planar geometry of the 1-naphthyl groups which are occupied by π-conformation. The B ring (see Fig. 1) overlaps with another B ring at the distance of 2.60 Å, in the racemic : tt state. The steric repulsion between B rings, which are spatially crowded by neighboring atoms, can not relieved by small increases in ϕ_i and ϕ_{i+1}. On the other hand, in the case of meso : tt state, each 1-naphthyl ring is parallel to the neighboring ones, and directed in the same direction; the distance between neighboring planes is estimated to be 2.60—2.75 Å. This steric repulsion between neighboring planes can not be avoided by small increases in ϕ_i and ϕ_{i+1}, as in the racemic : tt state.

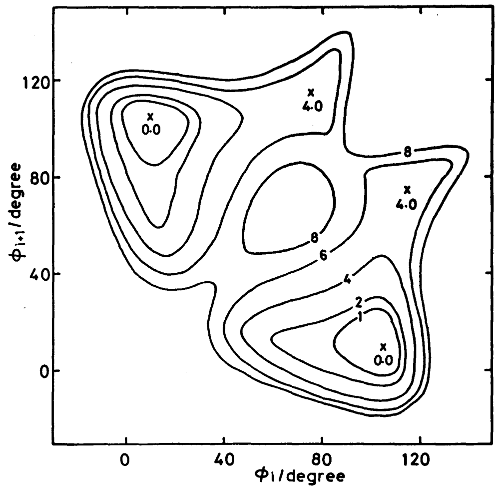

Fig. 2. Conformational energy contours for a meso dyad of PlVN calculated as functions of skeletal bond rotations ϕ_i, ϕ_{i+1}. Naphthyl group rotations fixed at X= 180° (π-conformation). A value of $\theta = 114°$ is used. Locations of minima are denoted by × and the energy contours are labeled in kcal mol^{-1} relative to the energy minium of the moso; tg conformation.

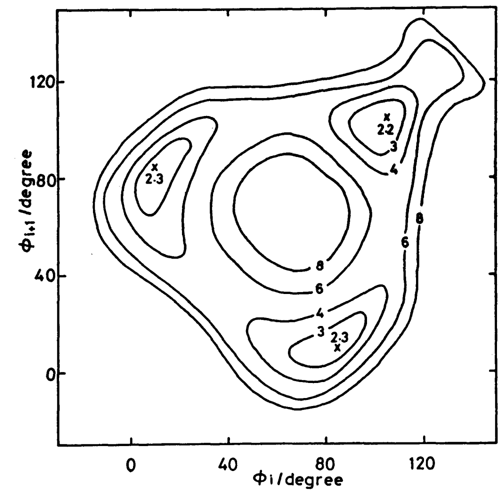

Fig. 3. Conformational energy contours for a racemic dyad of PlVN. A values of X= 180° and $\theta = 114°$ are used.

Figures 4 and 5 show the conformational energy maps for the meso and the racemic dyads of P1VN chain occupied by π-conformation, using $\theta = 120°$. The energies of the minima in Figs. 4 and 5 are expressed relative to the energy of the tt state of the racemic dyad. Six minima appear in Fig. 4 and four minima in Fig. 5. These minima are identified as tt, tg or gg. The $\bar{g}$ conformation is precluded, due to the interaction resulting from the planarity of the 1-naphthyl group.

In meso dyad, the minima at 80,120° or 120,80° in

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† 1 kcal mol^{-1}=4.184 kJ mol^{-1}.

†† 1 kcal mol^{-1} deg^{-2}=4.184 kJ mol^{-1} deg^{-2}.

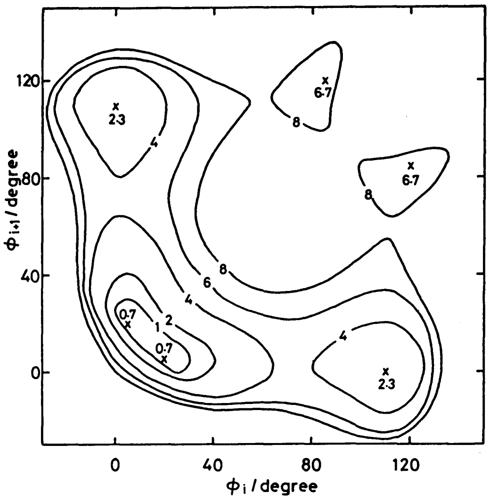

Fig. 4. Conformational energy contours for a meso dyad of P1VN, using X=180° and θ=120°. The energy contours are labeled in kcal mol^{-1} relative to the energy minimum of the racemic; tt ($\pi\pi$) at θ=120°.

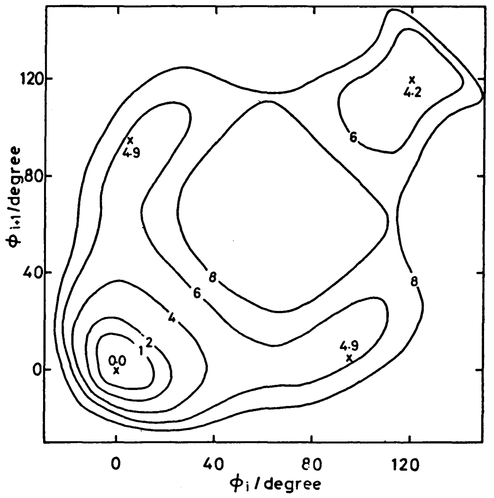

Fig. 5. Conformational energy contours for a racemic dyad of P1VN, using X=180° and θ=120°.

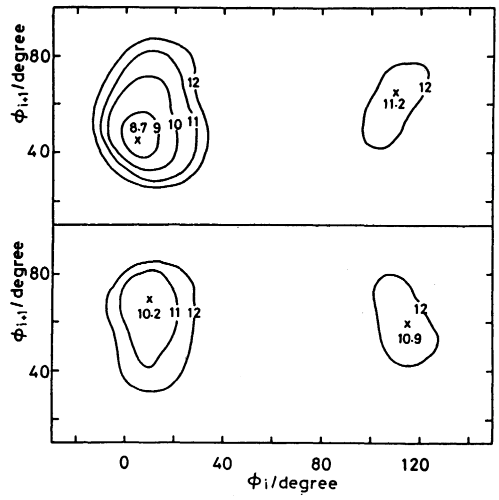

Fig. 6. Energy contours maps for (a) meso and (b) racemic dyads of P1VN, using X_{i-1}=180°, X_{i+1}=0° (o-conformation) and θ=114°. The energy contours were labeled in kcal mol^{-1} relative to the energy minimum of the meso; tg at θ=114° (see Fig. 2).

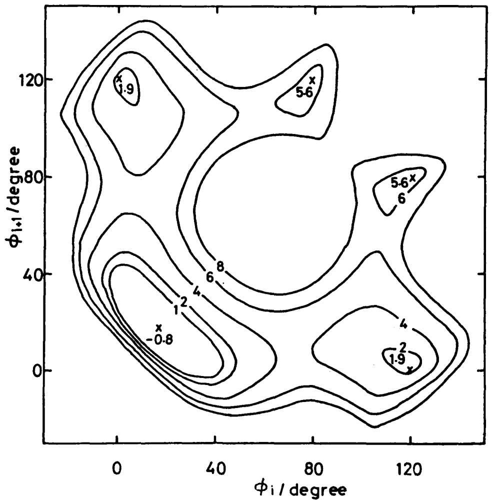

Fig. 7. Conformational energy contours for the meso dyad of P2VN($\pi\pi$), using θ=114°. The energy contours are labeled in kcal mol^{-1} relative to the energy minimum of the racemic; tt($\pi\pi$) at θ=114°.

Fig. 4 are isolated completely from the other minima. All minima are surrounded by the contour with 9 kcal mol^{-1}. In the energy maps of polystyrene chain, conformational energy contours of 5 kcal mol^{-1} are sufficient to surround all minima. The tt conformation is separated into two minima with a low energy barrier (<0.2 kcal mol^{-1}) between them. The distances between 1-naphthyl rings for ϕ_i,ϕ_{i+1}=0,0° are 2.73—3.37 Å. The steric repulsion in this case was more relaxed than that for θ=114°. Futhermore, ϕ_i,ϕ_{i+1} will displace somewhat from the perfect staggering (0,0°), and the energy then falls rapidly.

In racemic dyad, all minima could be surrounded by a contour with a larger value (about 8 kcal mol^{-1}). The minima for racemic : tt state appeared at smaller values of θ (about 116°) than those for the meso : tt state (about 118°). As described above, the neighboring 1-naphthyl ring in racemic : tt state was placed so as to approach to a part of 1-naphthyl ring (B ring), while 1-naphthyl ring in meso : tt state was placed in close proximity to the adjoining 1-naphthyl ring. The steric repulsion between neighboring 1-naphthyl rings in the racemic : tt state is smaller than that in the meso : tt state, and can be avoided by a small increase in θ.

Figures 6a and b show the energy contour maps for the meso(πo) and the racemic(πo) dyads, respectively. The energy contours are labeled in kcal mol^{-1} relative to the energy minimum of the meso tg (10,105°) at θ= 114°. The numbers of minima in Fig. 6 are less than that of P1VN occupied by π-conformation. Two minima for the meso and the racemic dyads are located at 5,45° and 110,65°, and at 10,70° and 115,60°, respectively. These minima values, as a function of ϕ_i and ϕ_{i+1}, have the lowest values at θ=114° over the range from 110° to 126°. However, these values are much higher than that of P1VN ($\pi\pi$). The o-conformation imposes steric overlap between the hydrogen at C(9) in

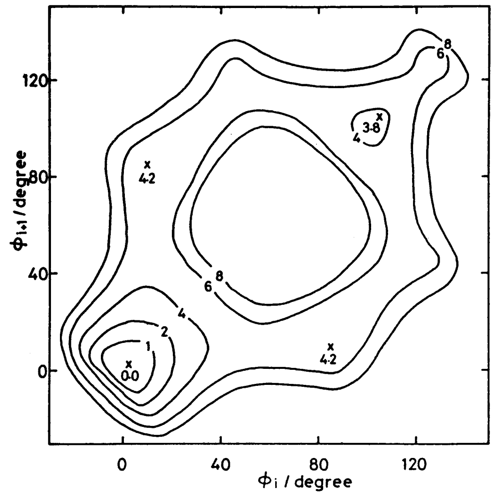

Fig. 8. Conformational energy contours for racemic dyad of P2VN($\pi\pi$), using $\theta=114°$.

a rotating 1-naphthyl ring and one of the methylene or α-carbons which belong to adjacent monomer unit, as reported in our previous paper.[1] Neither of the minima calculated here are assigned to RIS of skeletal bonds (t, g, and $\bar{g}$). The energy contour maps, in which all the RIS of side groups are in *o*-conformation, are not recorded in this paper, but the minimum values were remarkably large ($=20$ kcal mol^{-1}).

Figures 7 and 8 show the conformational energy contours for the meso and the racemic dyads of P2VN ($\pi\pi$), using $\theta=114°$. The energy surfaces in Figs. 7 and 8 were little influenced by the RIS of the side groups, and closely resembled that of polystyrene, except for the values of minima. For meso dyad, the distance between 2-naphthyl rings was 2.60—2.77 Å for $\phi_i,\phi_{i+1}=0,0°$. This distance is nearly equal to that of P1VN, but the minima of tt states for the meso have appeared over a range of θ(114°—120°). In P1VN chain, the steric interactions produced by the carbon and the hydrogen atoms in B ring are responsible for the larger conformational energy. On the other hand, in P2VN chain, the atoms in B ring are far apart from the backbone atoms (*e.g.*, αC or CH_2), and rapidly become detached from adjacent naphthyl rings if a small increase in ϕ_i and ϕ_{i+1} occurs. As reported in the previous paper,[1] there were no appreciable nonbonded interactions between the carbon atoms or hydrogen atoms bonded to carbon atoms in B ring of 2-naphthyl group and the main chain (or the neighboring side group). In racemic : tt, the B ring did not approach to the adjacent B ring, in contrast to that in P1VN chain.

The average energy $\langle E\rangle$, the partition function Z, and the average rotation angles $\langle\phi_i\rangle$, $\langle\phi_{i+1}\rangle$ were evaluated for each state with the use of energies calculated at intervals of 5° in ϕ_i and ϕ_{i+1}. These are given by

$$Z_s = \Sigma_i\Sigma_{i+1}\exp(-E_k/RT) \tag{4}$$

$$\langle E\rangle_s = Z_s^{-1}\Sigma_i\Sigma_{i+1}E_k\exp(-E_k/RT) \tag{5}$$

$$\langle\phi_j\rangle_s = Z_s^{-1}\,\Sigma_i\Sigma_{i+1}\phi_j\exp(-E_k/RT), \tag{6}$$

where the subscript k refers to each conformation (ϕ_i, ϕ_{i+1}) and j=i or i+1. The average energies $\langle E\rangle$ for P1VN and P2VN are plotted as functions of θ in Figs. 9 and 10, respectively. All values of $\langle E\rangle$ were evaluated relative to each meso : tg($\pi\pi$) state. Calculations were carried out for a temperature of 300 °K. The $\langle E\rangle$ for P1VN, except tt states, remained unaltered in the range of θ(114°—120°) and these curves showed precipitous rises of $\langle E\rangle$ beyond $\theta=120°$. The $\langle E\rangle$ of tt states had the lowest values at $\theta=122°$, as described above. In P2VN chain, all values had the lowest values at $\theta=118°$, and have the same curvature. The curves of polystyrene showed a similar tendency.

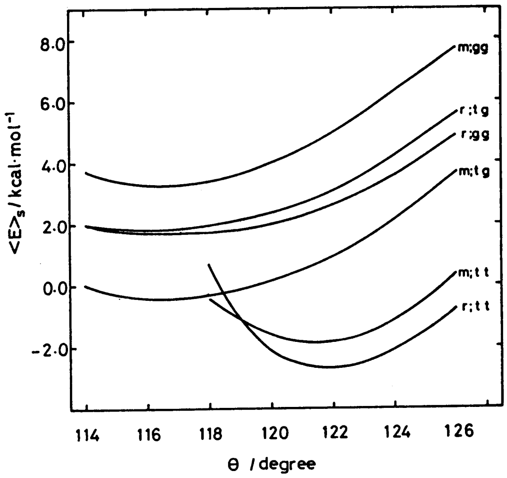

Fig. 9. The average energy $\langle E\rangle$ for P1VN were plotted as a function of the bond angle θ. All values were evaluated relative to the meso; tg($\pi\pi$) at $\theta=114°$.

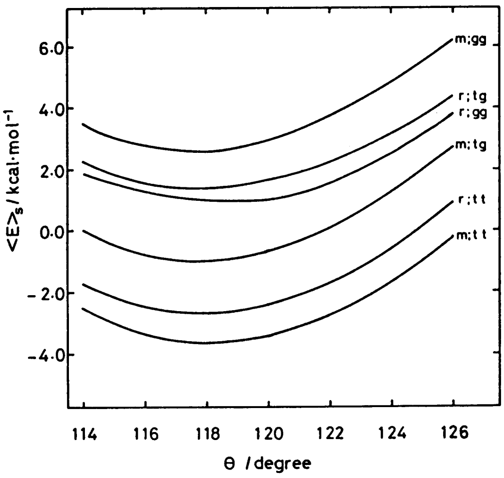

Fig. 10. The average energy $\langle E\rangle$ for P2VN. All values were evaluated relative to the meso; tg($\pi\pi$) at $\theta=114°$.

The lowest values appearing in Figs. 9 and 10 are assigned to the average energy of each RIS of skeletal bonds. The average energies $\langle E\rangle$ derived from Figs. 9 and 10, together with the averaged rotation angles $\langle\phi_i\rangle$, $\langle\phi_{i+1}\rangle$ are given in Table 2. The values of $\langle E\rangle$ were evaluated relative to that of the racemic : tt conformation. The meso : tt conformation in PVN and polystyrene had a lower energy. However, the rotational barrier of the aromatic group was much higher than

TABLE 2. AVERAGE ENERGIES[a] AND AVERAGE ROTATION ANGLES FOR EACH CONFORMATION

State	PS $\langle E\rangle$	PS $\langle\phi_i\rangle,\langle\phi_{i+1}\rangle$	P2VN $\langle E\rangle$				P2VN $\langle\phi_i\rangle,\langle\phi_{i+1}\rangle$	P1VN $\langle E\rangle$	P1VN $\langle\phi_i\rangle,\langle\phi_{i+1}\rangle$
			ππ	πo	oπ	oo	ππ	ππ	ππ
Meso : tt	1.07	20, 20	−0.98	−0.03	−0.03	−0.14	14, 14	0.85	12, 12
Meso : tg	1.19	5, 113	1.72	1.74	1.74	1.77	1, 116	2.32	7, 98
Meso : gg	4.36	95, 95	5.29	5.29	5.30	5.30	100, 100	6.10	96, 96
Racemic : tt	0.00	6, 6	0.00	0.47	0.47	0.78	−1, −1	0.00	−1, −1
Racemic : tg	3.32	13, 86	4.04	4.05	4.06	4.07	11, 95	4.53	8, 83
Racemic : gg	2.67	102, 102	3.67	3.67	3.67	3.66	114, 114	4.38	106, 106

a) All values are evaluated relative to each racemic : tt (ππ) state, in kcal mol^{-1} units.

TABLE 3. AVERAGE ENERGIES $\langle E\rangle$[a] FOR P1VN, P2VN, AND PS CHAIN

	Racemic tt	Racemic tg	Racemic gg	Meso tt	Meso tg	Meso gg
$\sigma=\infty$						
P1VN(ππ)	0.00	4.53	4.38	0.85	2.32	6.10
P2VN(ππ)	0.00	4.04	3.67	−0.98	1.72	5.29
PS	0.00	3.32	2.67	1.07	1.19	4.36
PS(Yoon)[b]	0.00	3.50	2.48	0.91	1.17	4.17
$\sigma=5.0$ Å						
P1VN(ππ)	0.00	2.16	1.49	1.45	0.43	3.48
P2VN(ππ)	0.00	2.66	2.26	1.56	0.82	3.73
PS	0.00	2.76	1.82	1.86	0.77	3.72
PS(Yoon)	0.00	2.95	1.67	1.61	0.73	3.36
$\sigma=3.9$ Å						
P1VN(ππ)	0.00	−0.71	−1.57	2.29	−2.64	0.47
P2VN(ππ)	0.00	1.97	1.58	3.62	0.20	3.03
PS	0.00	2.21	1.42	3.30	0.28	3.16
PS(Yoon)	0.00	2.67	0.98	2.61	0.30	2.66

a) All values are evaluated relative to each racemic : tt (ππ) state, in kcal mol^{-1} units. b) These values were calculated by Yoon *et al.* (Ref. 10).

that of the aromatic group in meso : tg conformation. This leads to a decrease of entropy in the planar conformation. Thus, at normal temperature, the meso : tt conformation seems to be unfavoured due to its larger free energy.

This problem can be resolved by a truncation procedure devised by Yoon *et al.*[6,10,11] This was followed so as to allow for the conformational dependence of solvent interaction. Beyond a certain distance, which is sufficient to permit the entry of the solvent molecules, the reduced interaction between aromatic groups will be replaced by the interaction between aromatic group and solvent, and the energy of the system levels off at this distance. Thus, the calculated energy remains constant at the value for $r=\sigma$ for all distances greater than a suitably chosen values of σ. The average energies $\langle E\rangle$, using $\sigma=5.0$ Å and 3.9 Å are given in Table 3, together with the $\langle E\rangle$ values for polystyrene calculated by Yoon.

In P2VN and PS chain, it is clear that racemic : tt conformation corresponds to the ground state (preferred conformation). The relationship of $\langle E\rangle_{tt}<\langle E\rangle_{gg}<\langle E\rangle_{tg}$ is found to hold, regardless of the value of σ chosen. The racemic : $t\bar{g}$ and $\bar{g}t$ conformations correspond to the excimer forming sites.[5] These conformations are unstable ones and have a energy of 7 kcal mol^{-1} higher than the lowest energy (tt state), since the conformations include the interaction between the aromatic groups. These results suggest that the statistical weights relating to $t\bar{g}$ and $\bar{g}t$ states are extremely small at normal temperature. Use of a truncation procedure shows that the conformational energy of meso : tt state is larger than that of meso : tg state, and that at $\sigma=3.9$ Å meso : tt conformation becomes the most unfavourable one in the meso dyad. Accordingly, the meso : tg conformation corresponds to the ground state, and the tt conformation corresponds to an excimer forming site, which is electronically stabilized under excimer formation.

In P1VN chain, the relative stability of each RIS in meso dyad is similar to those of P2VN and polystyrene, regardless of the value of σ chosen. Evidently, the meso : tg conformation corresponds to the ground state, and the conformational stability of it is higher than that of polystyrene and P2VN in meso dyad. On the other hand, the relative stability of each RIS in racemic dyad is strongly dependent on the value of σ : $\langle E\rangle_{gg}<\langle E\rangle_{tg}<\langle E\rangle_{tt}$ at $\sigma=3.9$ Å. The racemic : tt conformation is not necessarily the most stable one. The racemic: gg and tt conformations correspond to the ground state at $\sigma=3.9$ Å and $\sigma\geqq5.0$ Å, respectively. The racemic : $t\bar{g}$ and $\bar{g}t$ conformations are less favored states than tt, tg, and gg states; this is also found in P2VN and in polystyrene.

In PVN chain, the dual emission in excimer region was observed in solution. Gupta *et al.*[13] concluded that the two types of singlet excimers characterized by emission spectra of P1VN may consist of parallel and antiparallel conformations of pairs of 1-naphthyl groups. From the emission spectra of P2VN and its model compound (*meso*-1,1′-di-2-naphthyldiethylether) in solution, Schryver *et al.*[14] pointed out that the observation of a dual decay could be due to the relative orientation in the ground state of the naphthyl groups prior to excimer formation. The dual emission may be correlated with the RIS for side groups in PVN chain.

In P2VN chain, the dual emission in the excimer region may be correlated with two types of excimers site conformation differing in RIS for side group or site conformation differing in RIS for skeletal chain. Concerning the latter, meso : $\bar{g}\bar{g}$, meso : tt and racemic: $t\bar{g}(\bar{g}t)$ can be formed in a parallel sandwich arrangement

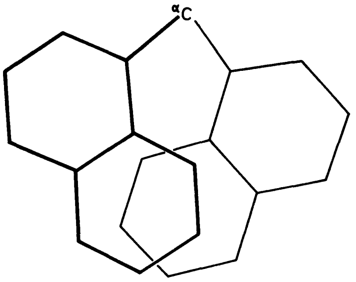

Fig. 11. A segment of a racemic; tt(ππ) of PlVN chain. l-naphthyl groups are parallel to the space. The hydrogens and methylene carbons are omitted.

of aromatic groups. However, the formations of the excimers consisting of those skeletal conformations, except meso : tt state, seem less likely, on the basis of our calculated results. The RIS of skeletal chain with respect to the excimer formation is occupied by the meso : tt conformation, and few racemic : t$\bar{g}$($\bar{g}$t) conformations occur. Since 2-naphthyl groups in P2VN chain are occupied by both *π*- and *o*-conformations,$^{1)}$ there are *ππ*, *oo*, *πo*, and *oπ* conformations for RIS of side groups in meso : tt state. The structure of *ππ* and *oo*-conformation are made up by the total superposition of 2-naphthyl groups, while 2-naphthyl groups in *πo* and *oπ* conformation are placed so as to approach near a part of 2-naphthyl group (A ring). It can be concluded that the dual emission observed in atactic P2VN chain should be attributed to the RIS of 2-naphthyl group in meso : tt state. The excimer forming site conformations are *ππ* and *oo* conformations; other conformations are *πo* and *oπ* ones.

Since 1-naphthyl groups in P1VN chain were limited to a preferred state (*π*-conformation),$^{1)}$ tt(*ππ*) conformation in meso dyad is the only conformation which forms the excimer. Other conformations are not detected in meso dyad. However, the racemic : tt(*ππ*) conformation can be formed in a sandwich arrangement of 1-naphthyl groups, whether that conformation is preferred or not. Figure 11 shows the relaxed molecular model of racemic: tt(*ππ*) state obtained by the force field method. This model structure fits with that used in the present paper. The racemic : tt conformation comes to be the excimer forming site conformation by deforming the bond angle of $\mathrm{C_{aromatic}}$–αC–$\mathrm{H_{methine}}$(about 7°). Accordingly, it is concluded that the dual emission in atactic P1VN chain should be attributed to the meso : tt(*ππ*) and racemic: tt(*ππ*) states. The meso : tt(*ππ*) and racemic : tt(*ππ*) states correspond to the parallel and antiparallel configurations proposed by Gupta,$^{13)}$ respectively.

The averaged rotation angles $\langle\phi_i\rangle$, $\langle\phi_{i+1}\rangle$ in Table 2 are independent of the values of σ chosen. The averaged rotational angles for the meso : tg in P1VN chain largely deviate from the perfect staggered conformation (0,120°). The values suggest that an isotactic P1VN chain forms a 4_1 helix. This conclusion is approximately consistent with the X-ray data on isotactic P1VN reported by Natta.$^{15)}$ Table 2 also shows that an isotactic P2VN chain forms a 3_1 helix.

References

1) K. Seki, Y. Ichimura, and Y. Imamura, *Macromolecules*’ **14**, 1831 (1981).

2) K. Seki, S. Mori, and Y. Imamura, *Bull. Chem. Soc. Jpn.*, **55**, 2739 (1982).

3) S. Ito, M. Yamamoto, and Y. Nishijima, *Polym. J.*, **13**, 791 (1981); C. David, M. Piens, and G. Geuskens, *Eur.Polym. J.*, **8**, 1019 (1972); M. Irie, T. Kamijo, M. Aikawa, T. Takemura, K. Hayashi, and H. Baba, *J. Phys. Chem.*, **81**, 1571 (1977); K. P. Ghiggino, R. D. Wright, and D. Phillips, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1499 (1978).

4) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).

5) C. W. Frank and L. A. Harrah, *J. Chem. Phys.*, **61**, 1526 (1974).

6) D. A. Brant and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 2791 (1965).

7) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).

8) P. R. Sundararajan and P. J. Flory, *J. Am. Chem. Soc.*, **96**, 5025 (1974).

9) U. W. Suter and P. J. Flory, *Macromolecules*, **8**, 765 (1975).

10) D. Y. Yoon, P. R. Sundararajan, and P. J. Flory, *Macromolecules*, **8**, 776 (1975).

11) P. R. Sundararajan, *Macromolecules*, **13**, 512 (1980).

12) R. W. G. Wyckoff, "Crystal Structures," Interscience, New York, London (1971), Vol. 6, Part 2, p. 383.

13) A. Gupta, R. Liang, J. Moacanin, D. Kliger, R. Goldbeck, J. Horwitz, and V. M. Miskowski, *Eur. Polym. J.*, **17**, 485 (1981).

14) F. C. De Schryver, K. Demeyer, M. van der Auweraer, and E. Quanten, *Ann. N. Y. Acad. Sci.*, **366**, 93 (1981).

15) G. Natta, *Makromol. Chem.*, **35**, 94 (1960); G. Natta, P. Corradini, and I. W. Bassi, *Gazz. Chim. Ital.*, **89**, 784 (1959).