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Conformational Characteristics of Poly(vinyl fluoride), Poly(fluoromethylene), and Poly(trifluoroethylene)

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ABSTRACT: Conformational energy estimates are employed to determine the conformational characteristics of poly(vinyl fluoride) (PVF), poly(fluoromethylene) (PFM), and poly(trifluoroethylene) (PTF_3). Effects of stereoconfiguration and, in the case of PVF and PTF_3, the presence of head-to-head:tail-to-tail (H-H:T-T) defect structures are considered. Rotational isomeric state models are developed for these polymers and used to calculate their unperturbed dimensions, dipole moments, and conformational entropies. The calculated results are compared to corresponding values found for poly(vinylidene fluoride), poly(tetrafluoroethylene), and polyethylene, and the equilibrium flexibilities of PVF, PFM, and PTF_3 are discussed on this basis.

During the course of our studies concerning the ^{13}C NMR chemical shifts of vinyl polymers we became interested in understanding the ^{13}C chemical shifts observed in the fluorinated polymers poly(tetrafluoroethylene) (PTFE), poly(vinylidene fluoride) (PVF_2), poly(vinyl fluoride) (PVF), poly(fluoromethylene) (PFM), and poly(trifluoroethylene) (PTF_3). We have demonstrated in hydrocarbon polymers, such as poly(propylene),[1,2] ethylene–propylene copolymers,[3,4] polystyrene,[5] etc., and in a chlorine-substituted vinyl polymer [poly(vinyl chloride)[6]], that the chemical shift of a given carbon atom depends on the frequency with which it is involved in three bond gauche or γ interactions[7-11] with other carbon or chlorine atoms.

Each γ interaction produces an upfield chemical shift on the order of 3–5 ppm. Enumeration of the number and kind of γ interactions involving a given carbon atom permits[11] a determination of its relative ^{13}C chemical shift. Bond rotation probabilities obtained from the rotational isomeric state (RIS) model[12,13] of a polymer chain lead to just such an accounting of possible γ interactions.

With knowledge of the conformational characteristics of these polymers it was possible to understand their stereosequence-dependent ^{13}C chemical shifts. Before the same approach can be attempted for fluorinated polymers, we must possess information concerning their conformational characteristics.

The conformational characteristics of PTFE[14] and PVF_2[15] have been determined through approximate potential energy estimates[16] and checked against experimentally determined unperturbed dimensions[17,18] and dipole moments.[14] However, neither PVF nor PFM nor PTF_3 have been studied from a conformational point of view. Such a study is described in this report, where the conformational energies of PVF, PFM, and PTF_3 chain fragments of various stereosequence are calculated, and where the possibility of head-to-head:tail-to-tail (H-H:T-T) addition of monomer units in PVF and PTF_3 is permitted and considered. From the conformational energies, RIS models are developed, and the conformationally sensitive properties $\langle r^2 \rangle_0$ and $\langle \mu^2 \rangle_0$, i.e., the mean-square unperturbed dimensions and dipole moments, and the conformational entropies, S_c, are calculated.

Conformational Energy Calculations

Portions of PVF (PTF_3) and PFM chains whose conformations depend on one or both of two neighboring bond rotation angles are illustrated in Figure 1. For PVF

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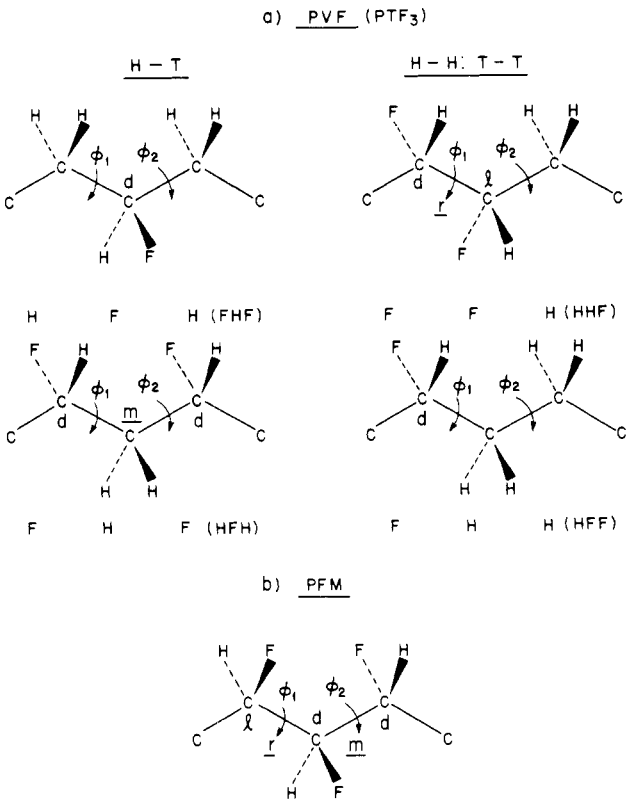

Figure 1. (a) PVF (PTF_3) chain fragments. CH_2 are replaced by CF_2 for PTF_3. (b) PFM chain fragments.

(PTF_3) both head-to-tail (H-T) HFH,FHF (FHF,HFH) and H-H:T-T FFH ↔ HFF,HHF ↔ FHH (HHF ↔ FHH,FFH ↔ HFF) chain fragments were considered. Conformational energies were calculated for each of these fragments as a function of the rotation angles ϕ_1 and ϕ_2, using the approximate potential energy functions[16,19] previously employed[14,15] in the analysis of the conformational characteristics of PVF_2 and PTFE.

An intrinsic threefold torsional potential with a barrier height of 3.0 kcal/mol is assumed to separate three rotational minima at ϕ_1 or ϕ_2 = 0 (trans, t), ±120° (gauche ±, g±). A 6–12 potential describes nonbonded van der Waals interactions, and partial charges[15] of ±0.2 esu are assigned to the C and F atoms, respectively, terminating C–F bonds to account for nonbonded electrostatic interactions. A dielectric constant ϵ = 6 was selected[15] to mediate the electrostatic interactions.

Bond lengths of 1.53, 1.36, and 1.10 Å were used for C–C, C–F, and C–H bonds, and the valence angles[20] ∠CCC = 112 (PVF), 116 (PTF_3), 117.5° (PFM), ∠HCF = ∠FCF = 106°, and ∠HCH = 109.5° were employed. Both rotation angles were stepped in 20° increments over their entire ranges.

Evaluation of RIS Models

Statistical weights $SW_{\alpha\beta}$ were evaluated for each of the nine pair-wise dependent rotational states $\alpha\beta$ = tt,-$tg^{\pm}$,$g^{\pm}t$,$g^{\pm}g^{\pm}$, and $g^{\pm}g^{\mp}$ from the calculated conformational energies. As an example,

$$SW_{g^+t} = \frac{\sum_{\phi_1=60°}^{180°} \sum_{\phi_2=-60°}^{60°} \exp[-E(\phi_1,\phi_2)/RT]}{\sum_{\phi_1=0}^{340°} \sum_{\phi_2=0}^{340°} \exp[-E(\phi_1,\phi_2)/RT]}$$

where the sums in both numerator and denominator contain only terms whose energies $E(\phi_1,\phi_2)$ are within 5.0 kcal/mol of the lowest energy conformation (ϕ_1,ϕ_2) found.

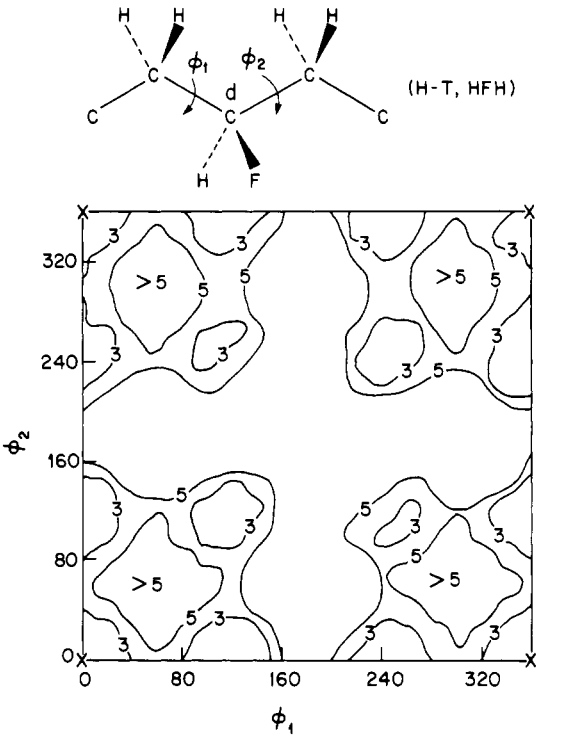

Figure 2. Conformational energy map for the HFH fragment in H-T PVF. Contours are in kcal/mol of fragment relative to the lowest energy conformation denoted by ×.

Statistical weight matrices U were then constructed at a given temperature. For PVF, as an example,

$$U_{HFH} = \begin{array}{c|ccc} \phi_1\backslash\phi_2 & t & g^+ & g^- \\ \hline t & SW_{tt} & SW_{tg^+} & SW_{tg^-} \\ g^+ & SW_{g^+t} & SW_{g^+g^+} & SW_{g^+g^-} \\ g^- & SW_{g^-t} & SW_{g^-g^+} & SW_{g^-g^-} \end{array}$$

One such statistical weight matrix was constructed for each different chain fragment (see Figure 1) considered in PVF, PFM, and PTF_3 at T = 0, 50, 100, 150, and 200 °C. These matrices define the RIS model appropriate to each polymer.

Calculation of Dimensions, Dipole Moments, and Conformational Entropies

Matrix multiplication techniques[13] were used to calculate mean-square end-to-end distances $\langle r^2\rangle_0$, dipole moments $\langle\mu^2\rangle_0$, and conformational entropies S_c of isolated and unperturbed PVF, PFM, and PTF_3 chains. A C–F bond dipole moment[21] of 1.8 D was used in the calculation of $\langle\mu^2\rangle_0$. Chains of 400–500 backbone bonds were considered. Each chain was generated a bond at a time by Monte-Carlo techniques and checked for the effects of stereosequence and (H-H:T-T) defect content at each bond addition. Ten Monte-Carlo chains were generated for each defect content and each degree of stereoregularity, and $\langle r^2\rangle_0$, $\langle\mu^2\rangle_0$, and S_c were averaged over the same ensemble of chains.

Calculated Results

Figures 2–6 present conformational energy maps for representative fragments of the PVF and PFM chains. Statistical weight matrices for all possible PVF, PFM, and PTF_3 chain fragments are given in the Appendix at T = 0, 50, 100, 150, 200 °C. The dimensions and dipole moments presented as the ratios $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle_0/nm^2$, where n is the number of bonds in the chain, l^2 is the square of the C–C bond length, and m^2 is the square of the C–F bond dipole moment ($^1/_2$ and $^3/_2$ the square for PVF and PTF_3), appear in Tables I and II. Temperature

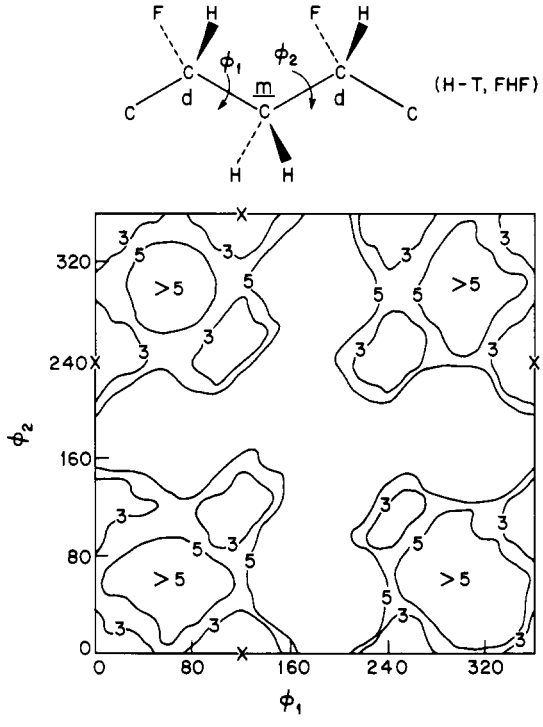

Figure 3. Same as Figure 2 except replace HFH with FHF.

TABLE I

$\frac{\langle r^2\rangle_0}{nl^2}$

and $\frac{\langle \mu^2\rangle_0}{nm^2}$

calculated for 400-500 Bond PVF and PTF_3 Chains as a Function of Stereoregularity and H-H:T-T Defect Content.

		PVF				PTF_3			
%H-H:T-T	P_m[a]	$\langle r^2\rangle_0/nl^2$		$\langle \mu^2\rangle_0/nm^2$		$\langle r^2\rangle_0/nl^2$		$\langle \mu^2\rangle_0/nm^2$	
0	0	7.2[b]	6.1[c]	1.28[b]	1.15[c]	9.9[b]	8.9[c]	0.54[b]	0.52[c]
"	.2	7.7	6.4	1.23	1.12	10.3	9.0	0.56	0.52
"	.4	8.0	6.5	1.20	1.10	10.5	9.0	0.57	0.52
"	.6	8.1	6.5	1.20	1.09	10.5	9.0	0.57	0.52
"	.8	7.8	6.3	1.22	1.12	10.3	9.0	0.56	0.52
"	1.0	7.2	6.1	1.28	1.16	9.9	8.9	0.54	0.52
10	0	7.2	6.0	1.06	1.00	10.8	9.5	0.43	0.43
"	.2	7.4	6.1	1.13	1.06	10.5	9.3	0.48	0.46
"	.4	7.7	6.3	1.08	1.01	10.9	9.4	0.48	0.45
"	.6	7.8	6.3	1.04	1.00	11.1	9.4	0.47	0.43
"	.8	7.6	6.3	1.05	0.99	11.0	9.5	0.47	0.44
"	1.0	7.2	6.0	1.08	1.02	10.7	9.4	0.44	0.44
20	0	7.1	6.0	0.90	0.90	11.6	9.9	0.35	0.37
"	.2	7.0	5.8	1.08	1.02	10.6	9.5	0.43	0.42
"	.4	7.3	6.0	1.00	0.95	11.1	9.7	0.42	0.40
"	.6	7.6	6.2	0.93	0.92	11.6	9.7	0.40	0.38
"	.8	7.5	6.1	0.91	0.89	11.8	9.9	0.38	0.38
"	1.0	7.2	6.0	0.93	0.92	11.5	9.9	0.37	0.36
30	0	7.1	5.9	0.79	0.80	12.4	10.4	0.30	0.32
"	.2	7.0	5.8	0.94	0.91	11.3	9.9	0.36	0.36
"	.4	7.1	5.9	0.94	0.93	11.3	9.8	0.37	0.37
"	.6	7.4	6.0	0.87	0.85	11.9	10.1	0.36	0.35
"	.8	7.4	6.0	0.80	0.82	12.4	10.3	0.33	0.32
"	1.0	7.1	5.9	0.79	0.82	12.3	10.2	0.30	0.32

a - Probability of a meso (m) dyad (see Figure 1(a))

b - T = 50°C

c - T = 150°C

coefficients of $\langle r^2\rangle_0$ and $\langle \mu^2\rangle_0$ are presented in Tables III and IV.

Discussion and Results

Both the calculated dimensions and dipole moments of PVF are virtually independent of stereosequence. Fur-

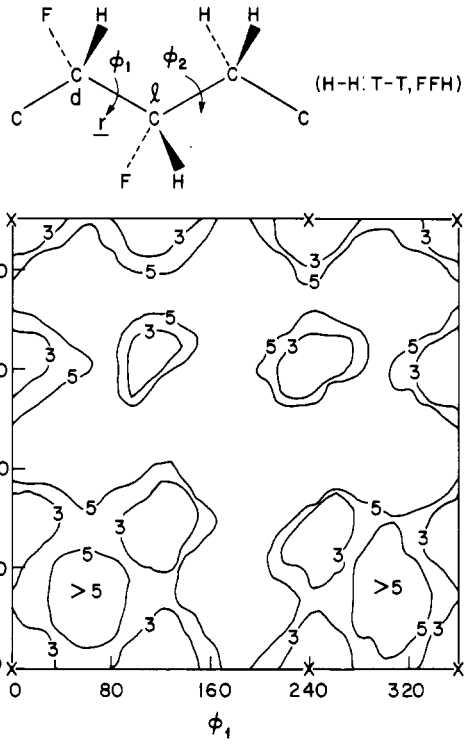

Figure 4. Same as Figure 2 except replace HFH with FFH and H-T with H-H:T-T.

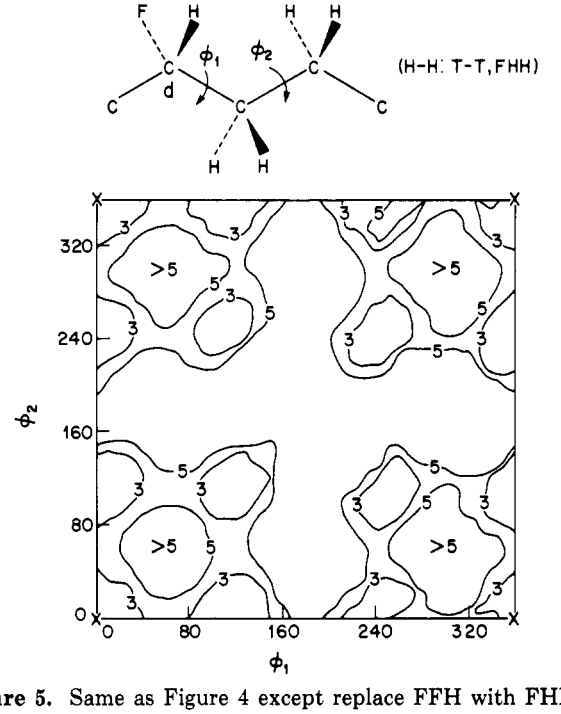

Figure 5. Same as Figure 4 except replace FFH with FHH.

Table II
$\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle_0/nm^2$
Calculated for 400 Bond PFM Chains as a Function of Stereoregularity

	$\langle r^2\rangle_0/nl^2$		$\langle \mu^2\rangle_0/nm$	
P_m[a]	50 °C	150 °C	50 °C	150 °C
0	13.3	10.4	2.11	1.67
0.2	10.5	8.54	1.58	1.39
0.4	8.57	7.30	1.17	1.07
0.6	7.07	6.06	0.86	0.83
0.8	5.81	5.13	0.58	0.60
1.0	5.01	4.95	0.36	0.40

[a] Probability of a meso (m) dyad (see Figure 1b).

TABLE III

$d\ln\langle r^2\rangle_0/dT$

and $d\ln\langle\mu^2\rangle_0/dT$

for PVF and PTF_3 Chains of 400-500 Bonds

of Varying Stereoregularities and
H-H:T-T Defect Contents

%H-T:T-T	Pm[a]	$(d\ln\langle r^2\rangle_0/dT)^b, K^{-1}$		$(d\ln\langle\mu^2\rangle_0/dT)^b, K^{-1}$	
		PVF	PTF_3	PVF	PTF_3
0	0	-.0017	-.0011	-.0010	-.0004
"	.2	-.0018	-.0013	-.0009	-.0007
"	.4	-.0021	-.0015	-.0009	-.0009
"	.6	-.0022	-.0015	-.0010	-.0009
"	.8	-.0021	-.0013	-.0009	-.0007
"	1.0	-.0017	-.0011	-.0010	-.0004
10	0	-.0018	-.0013	-.0006	0.0
"	.2	-.0019	-.0012	-.0006	-.0004
"	.4	-.0020	-.0015	-.0007	-.0006
"	.6	-.0021	-.0017	-.0004	-.0009
"	.8	-.0019	-.0015	-.0006	-.0007
"	1.0	-.0018	-.0013	-.0006	0.0
20	0	-.0017	-.0016	0.0	+.0006
"	.2	-.0019	-.0011	-.0006	-.0002
"	.4	-.0020	-.0013	-.0005	-.0005
"	.6	-.0020	-.0018	-.0001	-.0005
"	.8	-.0021	-.0018	-.0002	0.0
"	1.0	-.0018	-.0015	-.0001	-.0003
30	0	-.0018	-.0018	+.0001	+.0006
"	.2	-.0019	-.0013	-.0003	0.0
"	.4	-.0018	-.0014	-.0001	0.0
"	.6	-.0021	-.0016	-.0002	-.0003
"	.8	-.0021	-.0019	+.0002	-.0003
"	1.0	-.0018	-.0019	+.0004	+.0006

a - Probability of meso (m) dyad (see Figure 1(a))

b - dT = 150-50 = 100°C

Table IV
d ln $\langle r^2\rangle_0/dT$ and d ln $\langle\mu^2\rangle_0/dT$
for 400 Bond PFM Chains of Differing Stereoregularity

P_n[a]	d ln $\langle r^2\rangle_0$/ dT,[b] K^{-1}	d ln $\langle\mu^2\rangle_0$/ dT,[b] K^{-1}
0	−0.0024	−0.0023
0.2	−0.0021	−0.0013
0.4	−0.0018	−0.0009
0.6	−0.0015	−0.0004
0.8	−0.0012	+0.0003
1.0	−0.0012	+0.0011

[a] Probability of meso (m) dyad (see Figure 1b). [b] dT = 150 − 50 = 100 °C.

thermore the dimensions are also insensitive to the level of H-H:T-T addition. The characteristic ratios CR = $\langle r^2\rangle_0/nl^2$ calculated for PVF do not vary more than 10–15% over the entire spectrum of stereoregularity even allowing for as many as 30% H-H:T-T additions. Dipole moment ratios CM = $\langle\mu^2\rangle_0/nm^2$, although independent of stereosequence, do decrease 20–25% as the H-H:T-T content reaches 20–30%.

Neither property can be usefully employed to determine PVF stereoregularity, and they both fail to exhibit any marked degree of sensitivity to H-H:T-T defect content. These two conformational properties cannot be expected to characterize the microstructure of PVF.

Table V
Comparison of Unperturbed Dimensions

polymer	CR[a]	d ln $\langle r^2\rangle_0/dT$[b]
PE[c]	6.7	−0.0011
PVF	6.0	−0.0020
PVF_2[c]	5.9	−0.0013
PFM	4.5-10.5[d]	−0.0012-0.0024[d]
PTF_3	9.5	−0.0020
PTFE[c]	30	−0.0009

[a] T = 150 °C. [b] Calculated for dT = 150 − 50 = 100 °C. [c] Experimentally confirmed.[13,14,17,18] [d] Range corresponds to P_m = 1.0–0.0.

Table VI
Conformational Entropies Calculated at 150 °C

polymer	S_c, eu/(mol bonds)
PE	1.8
PVF	(2.1-2.3)[a]
PVF_2	2.0
PFM	(1.9-2.6)[b]
PTF_3	(1.8-2.0)[c]
PTFE	1.4

[a] Corresponds to P_m = 0.0–1.0 and 0% H-H:T-T addition. [b] Corresponds to P_m = 1.0–0.0. [c] Corresponds to P_m = 1.0–0.0 and 0% H-H:T-T addition.

Both CR and CM are sensitive to chain stereoregularity in PFM. As the probability of meso (m) dyad placement decreases from 1.0 to 0.0, CR and CM increase 2–3- and 4–6-fold, respectively. Clearly, either property can be expected to successfully characterize the stereoregularity of PFM chains.

Neither CR nor CM are sensitive to chain stereoregularity in PTF_3. As for PVF chains, only CM is significantly affected by H-H:T-T addition and may possibly be used to characterize the defect content of PTF_3 chains.

Inspection of the statistical weight matrices of PVF (see Appendix) indicates that several conformations, or (ϕ_1,ϕ_2) pairs of bond rotations, are likely regardless of stereosequence or defect content. Also note the similarities among the conformational energy maps of PVF fragments (Figures 2–5) corresponding to both H-T and H-H:T-T addition of monomer units. The similar degree of conformational diversity among all possible PVF chain fragments produces the nearly constant dimensions calculated for PVF chains of any likely structure. These comments are also applicable to PTF_3, with the additional observation that the larger dimensions [CR = 9.5 (PTF_3), 6.0 (PVF)] result from a significant increase in the probability of the all-trans (t), planar zigzag conformation.

The PFM chain, on the other hand, increasingly prefers the extended tt conformation as the meso (m) placement of dyads decreases. (The all-meso chain prefers the $tg^{\pm}$,$g^{\pm}t$ conformations, which result in compact chain conformations.) Hence, the all-racemic (r) chain has dimensions 2–3 times as large as all-meso (m) PFM.

PVF, PFM, and PTF_3 are all expected to contract with increasing temperature as indicated by the temperature coefficients of the dimensions, d ln $\langle r^2\rangle_0/dT$, presented in Tables III and IV. Stereosequence and defect content have little effect on the ability of these polymer chains to adopt more compact conformations as the temperature is raised.

It may be of interest to compare the conformational characteristics of PVF, PFM and PTF_3 with those of PVF_2, PTFE, and polyethylene (PE) to learn how the increasing

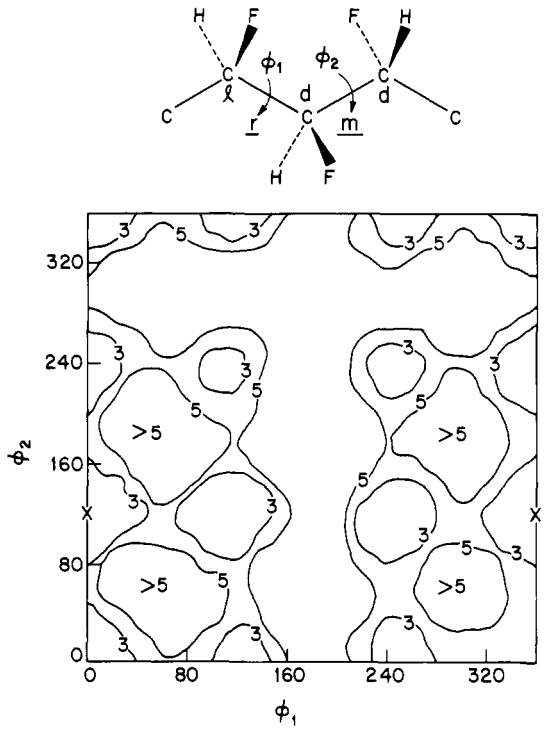

Figure 6. Conformational energy map for the *r*, *m* chain fragment of PFM. Contours are in kcal/mol of fragment relative to the lowest energy conformation denoted by ×.

fluorination of PE affects equilibrium chain extension. In Table V the calculated dimensions (CR) and their temperature coefficients are presented for PE, PVF, PFM, PVF_2, PTF_3, and PTFE. With the exceptions of the completely fluorinated member (PTFE) and predominantly isotactic PFM chains (with PM = 0.0–0.2), all members of this polymer series have dimensions which are remarkably similar, i.e., CR = 5–9. In addition, each polymer chain contracts with increasing temperature to adopt more compact conformations. This chain contraction is characterized by $d \ln \langle r^2 \rangle_0 / dT = -(0.001\text{–}0.002)\ K^{-1}$ for each of these polymers.

Although the conformational characteristics of PVF, PFM, and PTF_3 chains remain to be tested experimentally, it would appear that except for PTFE all of the polymers in this series possess comparable equilibrium extensions as manifested by their unperturbed dimensions. In addition, Table VI presents conformational entropies, S_c, calculated[22,23] at 150 °C for each polymer. Conformational entropy provides a measure of the number and frequency of occurrence of the various bond rotational states. Thus, CR and S_c, which are two distinctly different[24] probes of polymer chain conformations, both indicate that this series of polymers, with the exception of PTFE, possesses similar conformational characteristics.[25]

Acknowledgment. Happy Birthday Professor Flory.

Appendix: Statistical Weight Matrices[+] for PVF, PFM, and PTF_3 Chains at 0, 50, 100, 150, and 200 °C

PVF(H-T)

FHF(dd) =

$\phi_1 \backslash \phi_2$	t	g^+	g^-
t	.153[a]	.114	.202
	.151[b]	.115	.188
	.149[c]	.115	.179
	.148[d]	.114	.172
	.147[e]	.113	.167
g^+	.202	.068	.067
	.188	.074	.077
	.179	.078	.082
	.172	.082	.086
	.167	.085	.089
g^-	.116	.011	.067
	.118	.016	.073
	.119	.021	.078
	.119	.026	.081
	.119	.030	.083

PTF_3 (H-T)

HFH(dd) =

$\phi_1 \backslash \phi_2$	t	g^+	g^-
t	.358[a]	.261	.051
	.333[b]	.253	.064
	.313[c]	.244	.075
	.297[d]	.235	.084
	.284[e]	.227	.091
g^+	.051	.009	0.0
	.064	.015	0.0
	.075	.021	.001
	.084	.027	.001
	.091	.032	.002
g^-	.261	.001	.009
	.253	.003	.015
	.245	.005	.021
	.236	.008	.027
	.229	.010	.032

a – T = 0°C
b – T = 50°C
c – T = 100°C
d – T = 150°C
e – T = 200°C

PVF(H-T)

FHF(dl) =

$\phi_1\backslash\phi_2$	t	g^+	g^-
t	.347	.118	.092
	.301	.122	.096
	.271	.125	.099
	.249	.126	.102
	.233	.127	.103
g^+	.120	.112	.043
	.125	.114	.053
	.127	.115	.060
	.128	.115	.065
	.129	.115	.068
g^-	.099	.037	.032
	.105	.046	.038
	.108	.052	.043
	.110	.058	.047
	.112	.062	.051

HFH(d) =

$\phi_1\backslash\phi_2$	t	g^+	g^-
t	.314	.147	.163
	.276	.148	.165
	.251	.147	.164
	.235	.145	.162
	.223	.143	.160
g^+	.160	.047	.009
	.162	.055	.014
	.161	.062	.020
	.159	.067	.025
	.156	.071	.030
g^-	.114	.005	.041
	.122	.008	.050
	.126	.012	.057
	.129	.016	.062
	.130	.202	.067

PTF_3(H-T)

HFH(dl) =

$\phi_1\backslash\phi_2$	t	g^+	g^-
t	.629	.082	.065
	.539	.099	.082
	.472	.112	.095
	.423	.120	.103
	.386	.126	.110
g^+	.082	.001	.001
	.099	.002	.002
	.112	.004	.003
	.120	.006	.005
	.126	.008	.007
g^-	.065	.001	.074
	.082	.001	.094
	.095	.003	.107
	.103	.004	.116
	.110	.006	.122

FHF(d) =

$\phi_1\backslash\phi_2$	t	g^+	g^-
t	.151	.151	.219
	.151	.147	.205
	.149	.144	.195
	.149	.140	.187
	.148	.137	.181
g^+	.215	.066	.021
	.201	.076	.030
	.192	.084	.037
	.184	.089	.044
	.178	.092	.050
g^-	.075	.003	.099
	.083	.005	.102
	.088	.008	.104
	.093	.011	.104
	.096	.014	.105

Interchanging the second and third columns and rows of FHF(dd), FHF(dl), and HFH(d) yields FHF(ll), FHF(ld), and HFH(l), respectively. Interchange H and F for PTF_3.

PVF (H-H:T-T)

FFH(dl) =

$\phi_1\backslash\phi_2$	t	g^+	g^-
t	.195	.114	.098
	.184	.118	.100
	.176	.120	.101
	.171	.122	.101
	.167	.123	.101
g^+	.146	.126	.017
	.144	.125	.023
	.142	.124	.029
	.140	.123	.034
	.139	.122	.038
g^-	.199	.053	.052
	.188	.061	.057
	.181	.067	.060
	.175	.071	.063
	.170	.074	.066

FFH(dd) =

$\phi_1\backslash\phi_2$	t	g^+	g^-
t	.268	.067	.239
	.245	.074	.217
	.228	.079	.202
	.215	.083	.191
	.206	.086	.183
g^+	.111	.060	.039
	.115	.065	.048
	.118	.069	.056
	.120	.072	.062
	.121	.074	.066
g^-	.145	.013	.058
	.152	.019	.065
	.154	.024	.070
	.155	.028	.074
	.155	.032	.077

PTF_3(H-H:T-T)

HHF(dl) =

$\phi_1\backslash\phi_2$	t	g^+	g^-
	.255	.288	.018
	.246	.274	.027
t	.238	.261	.035
	.230	.249	.042
	.224	.239	.049
	.094	.009	0.0
	.107	.015	0.0
g^+	.116	.021	.001
	.122	.027	.001
	.127	.033	.002
	.294	.003	.039
	.275	.007	.050
g^-	.259	.011	.060
	.246	.015	.067
	.235	.020	.073

HHF(dd) =

	t	g^+	g^-
	.399	.107	.119
	.357	.117	.126
t	.326	.124	.131
	.302	.128	.134
	.284	.131	.136
	.230	.005	.002
	.225	.010	.004
g^+	.219	.015	.006
	.213	.020	.009
	.207	.024	.012
	.086	0.0	.052
	.097	0.0	.065
g^-	.105	.001	.074
	.110	.002	.082
	.114	.002	.088

Interchanging the second and third columns and rows of FFH(dl) and FFH(dd) yields FFH(ld) and FFH(ll). Each of the HFF matrices can be obtained from the appropriate FFH matrix via total interchange of elements. As an example, FHH(dd)[I,J]=FFH(dd)[J,I]. Interchange H and F for PTF_3.

PVF (H-H:T-T)

FHH(d) =

$\phi_1\backslash\phi_2$	t	g^+	g^-
	.270	.116	.140
	.245	.118	.143
t	.226	.119	.143
	.213	.119	.142
	.203	.120	.140
	.143	.074	.025
	.140	.081	.033
g^+	.138	.086	.041
	.136	.090	.047
	.135	.092	.052
	.122	.025	.085
	.117	.033	.090
g^-	.114	.040	.093
	.113	.046	.094
	.112	.051	.095

PTF_3 (H-T:T-T)

HFF(d) =

	t	g^+	g^-
	.432	.157	.067
	.382	.164	.080
t	.345	.166	.089
	.317	.167	.096
	.295	.166	.102
	.122	.009	.001
	.132	.014	.003
g^+	.137	.020	.005
	.141	.026	.007
	.143	.031	.009
	.172	.003	.037
	.175	.005	.046
g^-	.176	.008	.054
	.174	.012	.061
	.173	.015	.067

FHH(l) is obtained from FHH(d) by interchanging second and third columns and rows, and HHF(d) and HHF(l) are obtained by a total interchange (I,J→J,I) of the elements of FHH(d) and FHH(l). Interchange H and F for PTF_3.

PFM

	$\phi_1\backslash\phi_2$	t	g^+	g^-
		.036	.028	.257
		.045	.037	.237
	t	.053	.045	.221
		.059	.052	.208
		.065	.058	.198
lll =		.314	.074	.161
		.283	.083	.165
		.259	.090	.166
	g^+	.241	.095	.166
		.227	.098	.165
		.042	.003	.085
		.052	.005	.097
	g^-	.060	.008	.098
		.066	.011	.102
		.071	.014	.104

	$\phi_1\backslash\phi_2$	t	g^+	g^-
		.321	.129	.119
		.291	.134	.123
	t	.268	.137	.125
		.251	.138	.125
		.238	.139	.125
ldl =		.178	.030	.006
		.174	.039	.009
	g^+	.169	.047	.013
		.165	.054	.017
		.161	.060	.021
		.173	.014	.030
		.170	.021	.039
	g^-	.167	.028	.046
		.164	.034	.052
		.161	.039	.056

	$\phi_1\backslash\phi_2$	t	g^+	g^-
		.218	.312	.084
		.207	.283	.093
	t	.198	.262	.098
		.191	.245	.102
		.184	.233	.105
ldd =		.024	.183	.006
		.032	.177	.011
	g^+	.040	.172	.015
		.046	.166	.020
		.051	.161	.025
		.093	.069	.011
	g^-	.100	.080	.017
		.105	.088	.022
		.108	.094	.028
		.110	.098	.033

	$\phi_1\backslash\phi_2$	t	g^+	g^-
		.214	.016	.060
		.205	.023	.071
	t	.197	.029	.079
		.190	.035	.085
		.184	.039	.090
ldd =		.355	.156	.061
		.319	.154	.073
	g^+	.293	.150	.083
		.274	.146	.090
		.258	.142	.095
		.120	.006	.012
		.126	.010	.019
	g^-	.129	.015	.025
		.131	.019	.030
		.132	.024	.036

Interchanging second and third columns and rows of lll, ldl, ldd, and lld yields ddd, dld, dll, and ddl, respectively.

+ In the calculation of conformational entropies, S_c, all elements of each statistical weight matrix must be divided by the largest element corresponding to a given temperature. As an example, the elements of FHF(dd) (PVF) must be divided by .153, .151, .149, .148, and .147 when calculating S_c at T = 0, 50, 100, 150 and 200°C, respectively.

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(24) **Note Added in Proof**: After completion of the present work the author discovered conformational energy calculations performed previously on PTF_3 by R. R. Kolda and J. B. Lando [*J. Macromol. Sci., Phys.*, 11, 21 (1975)]. These authors treated helical conformations only and the effects of H-H:T-T defects on helix stability.