A molecular mechanics study on conformations of piezoelectric copolymers of vinylidene cyanide

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A molecular mechanics calculation has been applied to investigate conformational characteristics of highly alternating copolymers of vinylidene cyanide with vinyl acetate and methyl methacrylate. The former shows high piezoelectricity, while the latter has quite low piezoelectricity. It was found that the main-chain conformations depend on the configurations of the main chain as well as the conformations of the side chains. Both copolymers were found to take *trans*-rich conformations around the $C(CN)_2$–CH_2 bond. The vinyl acetate copolymer takes predominantly the *trans* conformation around the CH_2–$CH(OCOCH_3)$ bond. The methyl methacrylate copolymer also takes the *trans*-rich conformation around the CH_2–$C(COOCH_3)(CH_3)$ bond, but the fraction of *trans* conformer is not larger than that around the corresponding bond in the vinyl acetate copolymer. It was suggested that the main-chain conformation of vinylidene cyanide copolymers before drawing/poling treatments is one possible important factor determining the piezoelectric activity of these copolymers.

(Keywords: poly(vinylidene cyanide-*co*-vinyl acetate); poly(vinylidene cyanide-*co*-methyl methacrylate); conformation; piezoelectricity; molecular mechanics)

INTRODUCTION

The amorphous copolymer of vinylidene cyanide and vinyl acetate (P(VDCN/VAc)) has received much attention because of its high piezoelectricity[1]. In previous papers[2,3], ^1H and ^{13}C n.m.r. were successfully applied to elucidate the microstructure and conformation of P(VDCN/VAc) with monomer-unit composition VDCN:VAc = 1:1, where it was found that P(VDCN/VAc) is a highly alternating copolymer with atactic configuration with respect to the VAc side-chain.

Besides microstructure, the molecular conformation is an essential factor in determining the piezoelectricity of P(VDCN/VAc). If the main chain takes an all-*trans* conformation, P(VDCN/VAc) is expected to show high piezoelectricity[4]. It was also found from ^1H n.m.r. spin analysis that P(VDCN/VAc) takes the *trans*-rich conformation around the CH_2–$CH(OCOCH_3)$ bond in polar solvents[4]. The conformation around the $C(CN)_2$–CH_2 bond could not be determined experimentally due to lack of a vicinal proton spin–spin system.

The copolymer of vinylidene cyanide and methyl methacrylate (P(VDCN/MMA)) is also an amorphous and highly alternating VDCN copolymer with random configuration[5]. The differences in chemical structure between P(VDCN/VAc) and P(VDCN/MMA) are that in the latter the methoxycarbonyl group is substituted for the acetyl groups and the additive methyl group is attached to the α-carbon. Since P(VDCN/MMA) also has the C–C≡N dipole moment, which would contribute significantly to the piezoelectric activity of P(VDCN/VAc), piezoelectric activity comparable to that of P(VDCN/VAc) is expected for P(VDCN/MMA). But, under similar manufacturing conditions, the piezoelectric constant for P(VDCN/MMA)[6] is only $d_{31} \sim 0.2\,\mathrm{pC\,N^{-1}}$, which is one thirty-fifth of that of P(VDCN/VAc). The microstructures of both copolymers do not differ from each other[5]. Thus, a conformational effect is supposed to be important for the attainment of high piezoelectricity in VDCN copolymers. Unfortunately, P(VDCN/MMA) has no proton spin system, which gives information concerning the main-chain conformation.

In this paper, the molecular mechanics method is used to elucidate the conformational features of P(VDCN/MMA) as well as P(VDCN/VAc). At present molecular mechanics methods are widely used for the study of the stable conformations of molecules. In these methods, conformational energy is calculated using an empirical force field. The reason for the large difference in piezoelectric activity between P(VDCN/VAc) and P(VDCN/MMA) will be discussed on the basis of conformational analysis.

EXPERIMENTAL

Syndiotactic and isotactic alternating copolymer sequences of six monomer units were taken in the calculation as the model polymer chains for P(VDCN/VAc) and P(VDCN/MMA), as shown in *Figures 1* and *2*. In order to change the conformation of these sequences, one of three values, 60° (*gauche*, *G*), 180° (*trans*, *T*) and 300° (another *gauche*, *G'*), was assigned independently to each of the four central torsion angles designated by θ_1, θ_2, θ_3 and θ_4 in *Figures 1* and *2*. Here, a positive sign for the torsion angles indicates the right-handed screw. The conformers around the other main-chain C–C bonds were assumed to be *trans*. Hereafter, the conformation of the model will be indicated simply by capitals. For example, *GTTT* indicates the conformation with torsion

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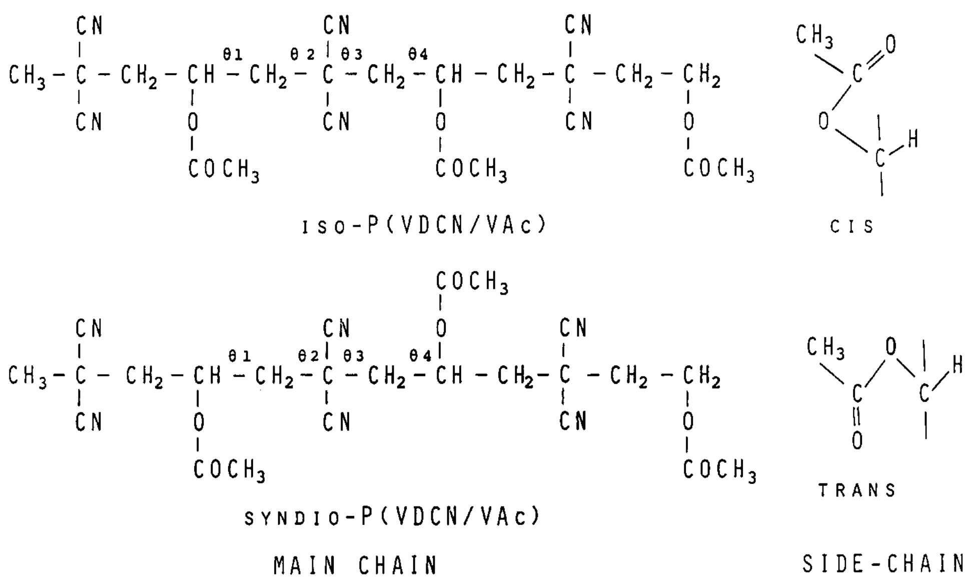

Figure 1 Model compounds of isotactic and syndiotactic P(VDCN/VAc)

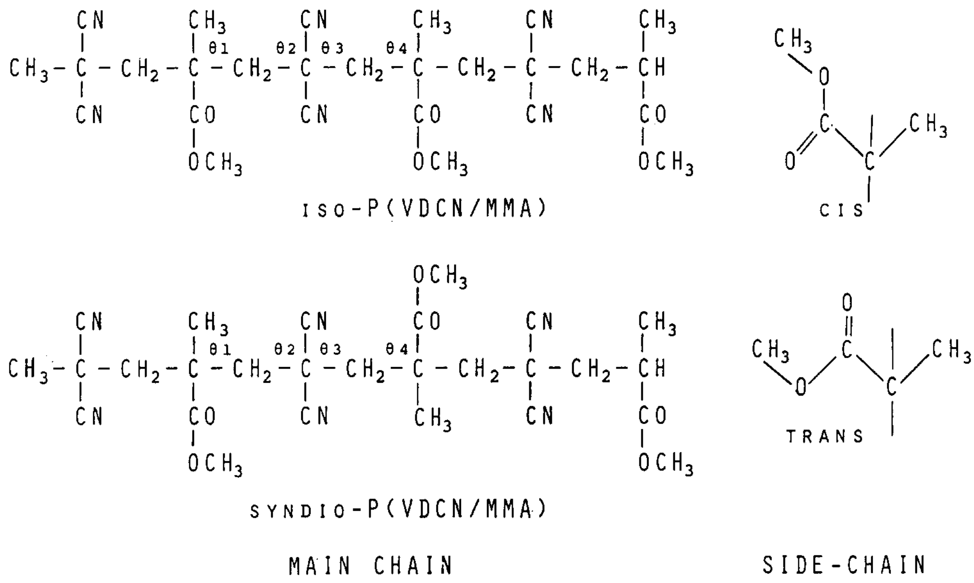

Figure 2 Model compounds of isotactic and syndiotactic P(VDCN/MMA)

angles of $(\theta_1, \theta_2, \theta_3, \theta_4)=(G, T, T, T)$. Conformations including improbable successive *GG*, *GG'*, *G'G*, or *G'G'* sequences were omitted in the calculation.

By symmetry, there are several sets of equivalent conformations. For example, for the syndiotactic model *GTTT* is equivalent to *TTTG*, and for the isotactic model *GTTT* is equivalent to *TTTG'*. As a result, 12 conformations shown in *Tables 1* and *2* were considered for each of the isotactic and syndiotactic models of P(VDCN/VAc) and P(VDCN/MMA).

As the side-chain conformation of the VAc unit in P(VDCN/VAc), two planar models were assumed, as also shown in *Figure 1*. In these models the carbonyl double bond is *cis* or *trans* to the methine C–H bond. From conformational analysis based on the molecular mechanics calculations, these side-chain models were found to be stable conformations[7].

Similarly, as shown in *Figure 2*, two models were assumed as the side-chain conformation of the MMA unit in P(VDCN/MMA)[8]. In these two models, the ester group is planar with the bond O–CH *cis* to the carbonyl double bond. Throughout the remainder of this paper, we will refer to these models as, for example, iso(or syndio)-P(VDCN/VAc)-*cis*(or *trans*), which indicates the isotactic (or syndiotactic) P(VDCN/VAc) model with the side-chain conformation of *cis* (or *trans*).

The molecular mechanics calculations were performed on a HITAC M-280 computer at the Information Processing Center of Tokyo Institute of Technology and on a supercomputer HITAC M-680H at the Computer Center of the Institute for Molecular Science (Okazaki) using Allinger's MM2 program[9], which was modified to enable the calculation of conformational energy of a molecule consisting of up to 300 atoms. The total steric energy (E) of the MM2 force-field program is the sum of energies of bond stretching (E_c), angle bending (E_b), stretching–bending cross-term (E_s), Van der Waals interaction (E_v), torsion (E_t) and dipole–dipole interactions (E_d). The interaction E_v can be divided into the contributions from 1,4 non-bonded interaction and other

Table 1 Total energy and its components (kJ mol^{-1}) for P(VDCN/VAc) models

(a) Syndio-P(VDCN/VAc)-*cis*

					E_v			
	Total	E_c	E_b	E_s	1,4	other	E_t	E_d
TTG′T	232.56	15.05	46.00	4.66	84.61	−24.96	−29.14	136.34
TTTG′	232.67	14.50	41.55	4.68	82.89	−25.62	−25.62	135.74
TG′TG′	233.05	14.61	48.90	5.02	82.96	−26.37	−26.37	130.44
TTTG	234.87	14.45	40.07	4.56	82.87	−19.33	−26.42	138.66
TG′TG	234.91	14.72	45.47	4.76	85.55	−24.75	−24.79	133.95
G′TTG′	234.96	14.05	43.03	4.92	82.28	−20.61	−22.61	133.90
TGTG	237.66	14.64	45.00	4.76	84.78	−23.97	−24.08	136.53
GTTG	240.45	14.70	41.74	4.89	83.21	−17.87	−21.92	135.70
TGTG′	240.49	15.26	48.72	5.03	84.30	−25.22	−25.09	137.50
TTTT	240.65	15.78	44.36	4.74	83.55	−20.32	−30.38	142.93
GTTG′	240.79	14.47	45.11	5.05	82.99	−17.89	−24.23	135.29
TTGT	249.41	15.45	49.32	4.74	85.77	−23.96	−24.02	142.12
TTG′T (%)	100	6.5	19.8	2.0	36.4	−10.7	−12.5	58.6
					25.6			

(b) Syndio-P(VDCN/VAc)-*trans*

					E_v			
	Total	E_c	E_b	E_s	1,4	other	E_t	E_d
TTG′T	223.57	14.23	52.13	5.53	75.47	−18.13	−32.00	126.29
TTTT	224.74	14.46	50.41	5.55	74.62	−14.08	−33.52	127.30
TTGT	230.43	14.31	53.75	5.56	76.17	−17.90	−30.98	129.52
TTTG	232.97	14.65	52.03	5.72	75.93	−13.69	−31.89	130.23
TGTG	233.55	14.31	50.44	5.51	77.95	−18.74	−26.30	130.36
TG′TG	233.57	14.51	54.68	5.70	76.86	−15.61	−30.74	128.18
GTTG	238.63	14.73	52.03	5.80	77.20	−12.91	−29.43	131.20
TTTG′	241.47	14.85	64.46	5.98	76.81	−11.90	−32.40	123.68
TG′TG′	243.04	14.83	66.69	6.00	77.39	−14.54	−31.52	124.19
GTTG′	246.89	14.97	64.17	6.06	77.86	−9.83	−30.31	123.97
TGTG′	247.11	14.84	65.87	5.94	78.04	−14.48	−29.30	126.20
G′TTG′	258.96	15.42	79.24	6.50	78.18	−8.67	−33.81	122.10

(c) iso-P(VDCN/VAc)-*cis*

					E_v			
	Total	E_c	E_b	E_s	1,4	other	E_t	E_d
TG′TT	229.66	14.39	43.94	4.71	84.25	−27.67	−24.07	134.10
TTTG	234.00	14.54	42.19	4.77	82.05	−19.32	−26.83	136.59
GTTG	234.07	13.94	41.36	4.83	82.07	−17.98	−23.30	133.14
TTGT	235.70	15.20	46.92	4.76	84.76	−22.90	−27.96	134.93
TG′TG′	235.72	14.68	44.42	4.72	84.11	−23.51	−24.28	135.58
G′TTG	236.51	14.20	43.79	5.03	81.35	−18.61	−23.57	134.33
TTTG′	236.76	14.82	43.72	4.82	83.47	−19.32	−27.17	136.41
TTTT	266.93	15.42	40.80	4.55	82.70	−19.60	−29.65	142.70
TGTG	239.36	14.71	48.09	4.95	84.19	−23.18	−24.69	135.28
TTG′T	241.16	15.33	47.11	4.69	85.07	−27.71	−27.71	142.58
GTTG	241.51	14.41	43.21	4.94	83.38	−23.87	−23.87	136.82
TGTG′	243.22	15.22	48.44	4.90	84.35	−24.65	−24.65	138.49

(d) iso-P(VDCN/VAc)-*trans*

					E_v			
	Total	E_c	E_b	E_s	1,4	other	E_t	E_d
TTGT	226.53	14.38	54.08	5.65	75.25	−16.42	−32.79	126.37
TTTT	227.05	14.77	51.36	5.76	74.20	−12.39	−33.61	126.95
TTG′T	229.55	14.39	52.71	5.59	75.52	−17.52	−30.64	129.51
TG′TG′	231.22	14.40	50.38	5.54	77.57	−16.99	−27.95	128.28
TTTG′	231.60	14.39	51.64	5.66	75.90	−12.87	−31.76	128.64
TGTG′	236.13	14.70	53.66	5.73	77.43	−17.15	−28.07	129.84
GTTG′	240.44	14.66	52.69	5.80	77.53	−12.30	−29.46	131.50
TTTG	243.18	15.27	63.70	6.05	76.18	−10.92	−32.92	125.81
TG′TG	247.47	15.12	68.83	6.18	78.00	−13.10	−34.61	127.05
GTTG	249.65	15.35	64.39	6.17	77.79	−10.71	−30.47	127.12
TGTG	249.91	15.21	66.24	6.03	77.92	−13.98	−29.76	128.24
G′TTG′	260.64	15.75	77.51	6.48	78.22	−9.61	−31.65	123.94

Table 2 Total energy and its components (kJ mol^{-1}) for P(VDCN/MMA) models

(a) Syndio-P(VDCN/MMA)-*cis*

					E_{v}			
	Total	E_{c}	E_{b}	E_{s}	1,4	other	E_{t}	E_{d}
G′TTG′	333.47	21.99	68.69	6.91	102.10	−15.20	8.74	140.25
TGTG′	334.68	22.24	73.62	6.85	103.79	−23.67	11.35	140.50
TTTG	335.94	23.15	70.84	6.88	103.97	−14.65	9.13	136.62
TTTG′	336.33	22.31	70.78	6.91	101.89	−16.16	10.22	140.29
TTG′T	336.61	23.26	72.70	6.77	104.57	−19.57	13.09	135.78
GTTG	337.71	22.60	70.39	6.85	106.19	−13.42	9.49	135.62
TGTG	337.94	22.52	76.52	6.80	105.23	−22.56	11.92	137.50
GTTG′	338.85	22.28	71.42	6.95	103.38	−21.26	12.81	140.77
TTGT	340.95	22.75	75.74	6.85	103.38	−21.26	12.81	140.77
TG′TG′	340.17	22.70	75.72	6.88	103.88	−21.53	13.84	139.68
TTTT	342.01	23.53	70.87	6.94	101.63	−14.67	12.87	140.78
TG′TG	346.48	22.86	76.95	6.91	106.22	−23.18	16.14	140.57
G′TTG′ (%)	100	6.6	20.6	2.07	30.6	−4.6	2.6	42.1
					26.1			

(b) Syndio-P(VDCN/MMA)-*trans*

					E_{v}			
	Total	E_{c}	E_{b}	E_{s}	1,4	other	E_{t}	E_{d}
TGTG	331.67	22.41	73.62	7.09	102.85	−20.59	−0.69	146.97
TTGT	333.70	22.66	72.38	7.05	101.04	−18.72	−1.37	150.65
TGTG′	335.87	22.29	74.19	6.94	103.16	−20.57	3.42	146.45
TG′TG′	337.59	22.75	76.27	7.20	102.92	−19.21	6.40	141.26
G′TTG′	337.92	22.62	73.17	7.09	102.33	−14.24	7.78	139.26
TTTG′	338.64	22.67	72.10	7.04	101.39	−14.61	3.59	138.09
TTTG	338.76	22.85	70.48	7.16	101.63	−14.13	−0.24	151.01
GTTG	339.28	23.16	70.57	7.25	103.06	−12.22	1.50	145.96
GTTG′	340.28	22.96	72.27	7.20	102.33	−12.49	3.81	144.20
TG′TG	341.49	23.08	75.46	7.26	103.47	−17.79	4.39	145.62
TTTT	341.62	23.13	69.26	7.09	99.91	−14.00	−1.98	158.20
TTG′T	344.08	22.91	76.52	7.06	102.52	−21.87	3.51	153.41

(c) Iso-P(VDCN/MMA)-*cis*

					E_{v}			
	Total	E_{c}	E_{b}	E_{s}	1,4	other	E_{t}	E_{d}
G′TTG	330.22	22.35	66.70	6.82	102.54	−10.96	4.59	138.17
TGTG	331.48	22.65	72.03	6.85	103.62	−19.19	7.14	138.43
TTTG	332.59	22.81	68.23	6.72	102.63	−12.08	7.60	136.68
GTTG	334.83	22.51	67.21	6.77	104.77	−11.30	7.79	137.09
TG′TG	335.01	22.76	72.56	6.86	104.66	−23.03	9.65	141.56
TTTT	335.03	23.85	68.59	6.84	102.15	−14.77	8.99	139.38
TGTG′	335.88	22.62	75.17	6.88	105.70	−24.13	10.69	138.96
TTGT	338.00	22.96	73.62	6.74	103.36	−19.23	10.45	140.10
TTG′T	338.39	22.90	76.85	6.98	102.79	−21.17	11.38	138.65
TTTG′	341.26	22.68	71.96	6.89	104.23	−15.92	12.15	139.28
TG′TG′	341.30	23.26	74.94	6.87	106.01	−20.27	11.49	139.00
GTTG′	345.24	22.42	71.66	6.97	106.44	−15.12	13.50	139.37

(d) Iso-P(VDCN/MMA)-*trans*

					E_{v}			
	Total	E_{c}	E_{b}	E_{s}	1,4	other	E_{t}	E_{d}
TGTG	332.84	22.23	72.52	7.08	102.33	−21.17	2.11	146.07
TTG′T	334.14	22.60	72.09	6.99	101.67	−21.51	−0.87	153.18
TTTG	336.27	22.78	71.54	7.20	100.47	−16.04	1.94	148.37
TTGT	336.27	22.56	74.63	7.07	101.72	−20.00	2.30	147.99
TG′TG′	336.58	22.94	74.51	7.22	103.97	−19.90	4.03	143.83
GTTG	336.99	23.04	71.08	7.28	101.99	−14.95	4.77	143.79
G′TTG	337.04	22.83	72.42	7.33	101.26	−15.61	6.01	142.79
TGTG′	337.43	22.67	72.50	7.03	103.61	−21.28	1.86	151.05
TTTG′	339.40	22.90	69.71	7.15	101.77	−13.99	0.04	151.82
TG′TG	339.85	22.63	76.10	7.15	104.11	−22.54	7.28	145.11
TTTT	341.67	23.26	68.94	7.15	99.81	−14.55	−2.22	159.34
GTTG′	341.88	23.15	69.55	7.26	103.33	−12.82	2.59	148.82

Table 3 Fractions (%) of conformers of P(VDCN/VAc) model compounds at 86.5°C (359.5 K)

	Syndiotactic			Isotactic	
	cis	*trans*		*cis*	*trans*
TTTT	0.09	19.00	*TTTT*	0.53	14.37
TTTG	0.64	1.21	*TTTG′*	0.56	3.10
GTTT	0.64	1.21	*GTTT*	0.56	3.10
TTGT	0.00	2.82	*TTG′T*	0.13	6.22
TGTT	0.00	2.82	*TGTT*	0.13	6.22
TTTG′	1.34	0.07	*TTGT*	0.79	17.12
G′TTT	1.34	0.07	*TG′TT*	0.79	17.12
TTG′T	1.39	28.24	*TTTG*	1.40	0.07
TG′TT	1.39	28.24	*G′TTT*	1.40	0.07
TGTG	0.25	1.00	*TG′TG′*	0.79	3.55
GTGT	0.25	1.00	*GTGT*	0.79	3.55
GTTG	0.10	0.18	*GTTG*	1.37	0.01
TG′TG′	1.18	0.04	*G′TTG′*	1.37	0.01
G′TG′T	1.18	0.04	*TGTG*	0.23	0.01
G′TG′T	0.62	0.00	*G′TG′T*	0.23	0.01
TG′TG	0.63	0.99	*TGTG′*	0.06	0.69
GTG′T	0.63	0.99	*GTG′T*	0.06	0.69
GTTG′	0.09	0.01	*GTTG′*	0.11	0.16
G′TTG	0.09	0.01	*G′TTG*	0.60	0.00
TGTG′	0.10	0.01	*TG′TG*	6.00	0.02
G′TGT	0.10	0.01	*G′TGT*	6.00	0.02

non-bonded interactions. The details of MM2 programs and the nature of energy functions used in MM2 were described in Allinger's original paper[9] and the textbook written by Burkert and Allinger[10]. The value of total energy for each conformer was determined after the optimization of the structure.

RESULTS

The values of total energy and their components for the P(VDCN/VAc) and P(VDCN/MMA) models are tabulated in *Tables 1* and *2*, respectively. The conformers were arranged in order of magnitude of their total energies, i.e. the most stable and the least stable conformers were listed respectively at the top and the bottom of each table. It is clear that the relative stability of each conformer depends on the configuration as well as on the side-chain conformation. For the most stable conformations of the syndio-P(VDCN/VAc) and syndio-P(VDCN/MMA) models with a side chain of *cis* conformation, i.e. *TTG′T* and *G′TTG′*, respectively, the values of percentages of respective contributions were also listed at the bottom of *Tables 1a* and *2a*. The percentages of E_c, E_b, E_s and E_v (sum) for the *TTG′T* conformer of the syndio-P(VDCN/VAc) model are nearly equal to those for the *G′TTG′* conformer of the syndio-P(VDCN/MMA) model. The absolute values of E_c, E_s and E_d contributions of the syndio-P(VDCN/VAc) model are not very different from those of the syndio-P(VDCN/MMA) model. But, in general, the absolute values of total energy of the former model are significantly lower than those of the latter model.

The values of total energy of the former model are distributed more widely than those of the latter, indicating that energy differences among the conformers are large in the former. The values of E_b and E_v (1,4 interaction) of the latter are about 20–30 kJ mol^{-1} higher than the corresponding values of the former. In addition, the sign of E_t is opposite, namely negative for the former and positive or negative but nearly zero for almost all E_t values of the latter. These differences between P(VDCN/VAc) and P(VDCN/MMA) models are of course due to the differences in the side-chains of comonomer units, i.e. in the former only the carbonyl group is bonded to the main chain via the –O– spacer oxygen atom, while in the latter the bulky carbonyl group is directly bonded to the main-chain carbon to which bulky methyl group is also directly bonded and is producing a more crowded situation.

In *Tables 3* and *4* are shown the percentages of each conformer of both copolymer models. The fractions were calculated by assuming the Boltzmann distribution of conformers at the temperature of 359.5 K, which corresponds to the temperature of ^{1}H n.m.r. measurements. By employing this temperature, we can directly compare the calculated fractions of conformers of the P(VDCN/VAc) model with the observed ones of P(VDCN/VAc). In the case of the syndiotactic P(VDCN/VAc) model, the fractions of three conformers are overwhelmingly large, namely 56% *TTG′T* plus *TG′TT* and 19% *TTTT* with the *trans* side-chain conformation. The sum of them amounts to 75%. The fractions of similar conformers, i.e. *TTGT* plus *TG′TT* and *TTTT* are also large for the isotactic P(VDCN/VAc) model, but the sum of them is less than 50%. In the case of P(VDCN/MMA) models, there is no conformer that has an overwhelmingly large fraction. This result of course corresponds to the narrower distribution of the values of total energy, as described above. It is noteworthy that the major conformers of the isotactic P(VDCN/MMA) model have the *cis* side-chain conformation, not the *trans* one as found for the other models.

In order to clarify the preference of conformation around the respective bonds, the fractions of *T*, *G* and *G′* conformers were calculated for the two bonds in each model, by assuming also Boltzmann statistics. The results for the respective models with different side-chain conformations and for the models with *cis* and *trans* side-chain conformations are shown in *Tables 5* and *6*, respectively. It is clear that the preferred conformers

Table 4 Fractions (%) of conformers of P(VDCN/MMA) model compounds at 86.5°C (359.5 K)

	Syndiotactic			Isotactic	
	cis	*trans*		*cis*	*trans*
TTTT	0.39	0.45	*TTTT*	2.58	0.28
TTTG	3.01	1.17	*TTTG*	5.83	1.70
GTTT	3.01	1.17	*G′TTT*	5.83	1.70
TTGT	0.56	6.38	*TTGT*	0.95	1.70
TGTT	0.56	6.38	*TG′TT*	0.95	1.70
TTTG′	2.64	1.22	*TTTG′*	0.32	0.60
G′TTT	2.64	1.22	*GTTT*	0.32	0.60
TTG′T	2.40	0.20	*TTG′T*	0.84	2.75
TG′TT	2.40	0.20	*TGTT*	0.84	2.75
TGTG	1.54	12.58	*TG′TG′*	0.32	1.53
GTGT	1.54	12.58	*GTGT*	0.32	1.53
GTTG	1.67	0.98	*GTTG*	2.59	1.33
TG′TG′	0.52	1.73	*G′TTG′*	2.59	1.33
G′TG′T	0.52	1.73	*TGTG*	8.45	5.35
G′TG′T	6.89	1.55	*G′TG′T*	8.45	5.35
TG′TG	0.09	0.47	*TGTG′*	1.93	1.15
GTG′T	0.09	0.47	*GTG′T*	1.93	1.15
GTTG′	1.14	0.70	*GTTG′*	0.08	0.26
G′TTG	1.14	0.70	*G′TTG*	12.87	1.31
TGTG′	4.59	3.08	*TG′TG*	2.58	0.51
G′TGT	4.59	3.08	*G′TGT*	2.58	0.51

Table 5 Fractions (%) of conformers around the θ_3 and θ_4 bonds in syndiotactic and isotactic P(VDCN/VAc) and P(VDCN/MMA) models with *cis* and *trans* side-chain conformations

			Around θ_3 bond			Around θ_4 bond		
Model			*T*	*G*	*G'*	*T*	*G*	*G'*
P(VDCN/VAc)	Syndiotactic	*cis*	70.5	2.9	29.6	58.2	14.2	27.6
		trans	62.4	4.4	33.3	96.0	3.9	0.2
	Isotactic	*cis*	66.6	31.7	1.8	47.6	40.1	12.3
		trans	63.7	27.2	9.1	90.0	0.1	9.8
P(VDCN/MMA)	Syndiotactic	*cis*	76.5	16.2	7.3	64.2	25.5	10.3
		trans	57.9	38.0	4.1	58.3	27.4	14.3
	Isotactic	*cis*	76.2	6.1	17.7	40.3	51.2	8.5
		trans	62.5	10.3	27.3	58.7	28.0	13.3

Table 6 Fractions (%) of conformers around the θ_3 and θ_4 bonds in syndiotactic and isotactic P(VDCN/VAc) and P(VDCN/MMA) models

		Around θ_3 bond			Around θ_4 bond		
Model		*T*	*G*	*G'*	*T*	*G*	*G'*
P(VDCN/VAc)	Syndiotactic	63.4	4.2	32.5	90.1	5.1	4.8
	Isotactic	64.4	11.1	24.4	79.1	9.7	10.4
P(VDCN/MMA)	Syndiotactic	65.8	28.7	5.4	52.6	23.4	24.1
	Isotactic	70.2	7.6	22.3	45.6	42.5	11.9

around the θ_3 and θ_4 bonds of all model compounds are *T* irrespective of the side-chain configuration. The *T* conformer fraction around the θ_4 bond amounts to 90% and 79%, respectively, for the syndiotactic and isotactic P(VDCN/VAc) models. It has been found from ^{1}H n.m.r. analysis that the *T* conformer fraction around the θ_4 bond, namely the CH_2–$CH(OCOCH_3)$ bond, was 70.0% and 83.3%, respectively, for syndiotactic and isotactic P(VDCN/VAc) in dimethylsulphoxide solution. Thus, the results obtained from the molecular mechanics calculations agree well with those obtained by ^{1}H n.m.r. analysis, supporting the reasonableness of the force fields used for the calculations.

The molecular mechanics calculations can also predict the preferred conformers around the bonds that cannot be determined experimentally by n.m.r. due to the absence of usable spin systems. The calculations suggest that the preferred conformation around the $C(CN)_2$–CH_2 bond of P(VDCN/VAc) is also *T*, although the fraction of *gauche* conformers (*G* plus *G'*) is not small. The preferences for *T* conformer around the θ_3 and θ_4 bonds are also suggested for the P(VDCN/MMA) models. The fractions of *T* conformer around the θ_3 bond in the P(VDCN/MMA) models are comparable to those in the P(VDCN/VAc) models. In contrast, the fractions of *T* conformer around the θ_4 bond in the P(VDCN/MMA) models are significantly smaller than those in the P(VDCN/VAc) models.

DISCUSSION

Piezoelectric polymers would have a large dipole moment. The dipole orientation of amorphous polymers such as VDCN copolymers is achieved by the conformation of individual chains. If the main chains of VDCN copolymers take an *all*-trans conformation, the dipoles of the cyanide groups, which must be the main origin of piezoelectricity of these copolymers, align regularly. In the previous paper[4], we have shown by the calculation that all-*trans* P(VDCN/VAc) chain has a large dipole moment, which amounts to twice that of the other conformations with *gauche* bonds. Thus, the main-chain conformation plays an important role in producing the piezoelectric activity. The molecular mechanics calculations described in this work indicate that the P(VDCN/VAc) chain has higher tendency to take *trans*-rich conformations than the P(VDCN/MMA) chain. In other words, these calculations suggest that the former copolymer would show higher piezoelectric activity than the latter, in accordance with the experimental results, if the alignment of $C(CN)_2$ dipoles in a single chain of VDCN copolymer is in the film thickness direction. However, the molecular mechanics calculations indicate clearly that the *trans* conformation is not overwhelmingly stable for respective bonds in the P(VDCN/VAc) model chain and not unstable in the P(VDCN/MMA) model chain. The main-chain conformation of VDCN copolymers is one possible factor determining the piezoelectric activity of these copolymers, but other factors must be taken into consideration.

The dipolar alignment in the film thickness direction can be artificially induced by poling treatment. Here, we must point out an important factor, i.e. the chain flexibility or mobility. The VDCN copolymers show high piezoelectric activity only after drawing followed by poling treatments at a temperature just below their glass transition temperature[1]. The fraction of extended (*trans*) conformer may increase with drawing. When the films of P(VDCN/VAc) and P(VDCN/MMA) are drawn to the same extent, the former should still show higher piezoelectricity than the lattter, as the former has a higher fraction of *trans*-rich conformations. Poling under a d.c. electric field forces the transformation of the molecular arrangement in such a way as to orient the dipole moment parallel to the film thickness direction. Thus, the chain flexibility is important in determining the extent of dipole orientation, and thus the piezoelectricity attainable by poling treatments. The study of chain flexibility of VDCN copolymers is now in progress on the basis of molecular mechanics calculations.

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