Stereospecificity and Dipole Moment of Polymers. I. Dielectric Property of Polyvinyl Chloride Solution

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The properties of polyvinyl chloride (PVC) vary according to the temperature at which it is polymerized. Studies of the infrared absorption spectrum reveal that low-temperature polymerized PVC, compared with commercial PVC1), is rich in syndiotactic portion. Owing to their high crystallinity, however, most of the studies of stereospecific polymers have been limited to a consideration of their solid state properties, such as X-ray diffraction, infrared absorption spectrum and melting point. It is expected that molecules of isotactic, syndiotactic and atactic polymers, which are stereoisomers of each other, may take different shapes in solution and, therefore, give their solutions different porperties. However, not many reports on studies of the solutions of stereospecific polymers have yet been published. Danusso and his coworkers2,3) pointed out that the second virial coefficients of a toluene solution of isotactic polystyrene obtained from osmotic pressure measurements are different from that of atactic polystyrene. Differences in Flory temperature and in entropy parameter between isotactic and atactic polystyrene were reported by Wessling ėt al.4) New approaches in this field seem to be found in the study of tacticity through the measurement of the nuclear magnetic resonance absorption spectra of isotactic and syndiotactic polymethyl methacrylates in a chloroform solution5) and in the estimation of the tacticity of polyalkyl methacrylate from the reaction velocity of hydrolysis6).

The dipole moment of polar vinyl polymer is related to the orientation of monomer units carrying polar groups, and the observed moment is the statistical average over the molecular conformations. Its theoretical treatment was originally developed by Eyring7) and by Suzuki8) et al., and has been recently extended by Volkenstein9), Nagai10) and Suzuki11).

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Recently Pohl[12] et al. measured the dipole moments of isotactic, syndiotactic and atactic polymethyl methacrylates and found that their values differ.

With low-temperature polymerized PVC, one of the authors measured the viscosity, osmotic pressure and light scattering of a tetrahydrofuran solution and found that both the solvent-solute interaction parameter and the extension of the molecule are somewhat larger than those of commercial PVC[13].

For this report, the dielectric properties of both low-temperature polymerized and commercial PVC solutions were measured in order to discuss the relation between the dipole moment values and the tacticity of polymers.

Experimental

Samples.—Sample I is PVC obtained by radical polymerization carried out at −15°C, and sample II is commercial PVC obtained by radical polymerization at 58°C. Both samples were purified by being dissolved in tetrahydrofuran, precipitated by the addition of a large amount of methanol, and dried in vacuo to a constant weight.

Measurement of Dielectric Polarization and Method of Calculation. — The dielectric constants and densities of tetrahydrofuran solutions of samples I and II were measured and the average dipole moment per monomer unit was determined according to the generally accepted procedure[14].

$$p_2=p_1\{3\alpha/(\varepsilon_1-1)(\varepsilon_1+2)-\beta/d_1+1\} \qquad (1)$$

$$\mu=0.0128\sqrt{(P_2-[MR]_D)T}\ \mathrm{D} \qquad (2)$$

where $[MR]_D$ is the molcular refraction of the molecular unit.

The specific polarization p_2, determined by formula 1, proposed by Halverstadt-Kumler[15], multiplied by the molecular weight M of the monomer unit gives the molecular polarization, $P_2(=M\times p_2)$. Orientation polarization was obtained by subtracting $[MR]_D$ from P_2, and the dipole moment, μ, per monomer unit of polymer was determined by formula 2.

α and β in formula 1 are increments of the dielectric constant and the density of the solution respectively. When ε_1, ε_{12} and d_1, d_{12} denote the dielectric constants and the densities of the solvent and solution respectively, and w denotes the weight fraction of the solute, α and β will be given by:

$$\alpha=\{(\varepsilon_{12}-\varepsilon_1)/w\}_{\mathrm{Av}}$$

$$\beta=\{d_{12}-d_1)/w\}_{\mathrm{Av}}$$

P_1 in formula 1 is the specific polarization of the solvent given by

$$P_1=(\varepsilon_1-1)/(\varepsilon_1+2)d_1$$

The dielectric moment measurements were made at 500 kc/sec. by the heterodyne beat method. Details of the apparatus were given in a previous report[16].

The cell is composed of three concentric cylindrical platinum electrodes, the first and the third of which are earthed. The three-electrode system makes the shielding better and the capacity larger;

TABLE I. DIELECTRIC PROPERTY OF TETRAHYDROFURAN SOLUTION OF LOW-TEMPERATURE POLYMERIZED POLYVINYL CHLORIDE (SAMPLE I)

w	20°C		40°C	
	ε_{12}	d_{12}	ε_{12}	d_{12}
0.06144	8.153	0.9082	7.402	0.8877
0.04658	7.989	0.9028	7.295	0.8816
0.03730	7.850	0.8999	7.159	0.8782
0.02412	7.650	0.8926	7.008	0.8736
0	7.474($=\varepsilon_1$)	0.8863($=d_1$)	6.882($=\varepsilon_1$)	0.8650($=d_1$)

TABLE II. DIELECTRIC PROPERTY OF TETRAHYDROFURAN SOLUTION OF COMMERCIAL POLYVINYL CHLORIDE (SAMPLE II)

w	20°C		40°C	
	ε_{12}	d_{12}	ε_{12}	d_{12}
0.06778	8.123	0.9109	7.371	0.8897
0.05295	7.972	0.9064	7.265	0.8848
0.04190	7.856	0.9015	7.186	0.8802
0.02714	7.718	0.8962	7.064	0.8746
0	7.474($=\varepsilon_1$)	0.8863($=d_1$)	6.882($=\varepsilon_1$)	0.8650($=d_1$)

w: Weight fraction of polymer, ε_{12}: Dielectric constant of solution, d_{12}: Density of solution, ε_1: Dielectric constant of solvent, d_1: Density of solvent

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it is approroximately 75 $\mu\mu$F. Density was determined by means of a density bottle of a flask shape, the volume of which was approximately 10ml.

Meaurements were carried out at four concentrations between 2~7% for each sample at 20 and 40°C. Each solution was prepared by heating polymer and tetrahydrofran in a sealed glass ampoule for two hours at 100°C immediately before the measurement. The results are listed in Tables I, II and III. The errors in μ-values are estimated to be ± 0.02D.

Results and Discussion

Dipole Moment of Stereospecific Polymer.—The results in Table III show that the dipole moment per monomer unit of sample I is 1.39 D, and that of sample II is 1.31 D, both independent of the measurement temperature. This 6% decrease may be attributed to the decrease in the syndiotactic portion, although the values are apparent ones, affected by the interaction between the polymer and the polar solvent, tetrahydrofuran.

TABLE III. DIPOLE MOMENT OF POLYVINYL CHLORIDE IN TETRAHYDROFURAN

	Low-temperature polymerized PVC (sample I)		Commercial PVC (sample II)	
	20°C	40°C	20°C	40°C
p_1	0.7710	0.7655	0.7710	0.7655
α	10.839	8.503	9.329	7.140
β	0.358	0.354	0.369	0.362
p_2	0.8684	0.8260	0.8021	0.7588
P_2 (cc.)	54.28	51.63	50.13	47.43
μ (D)	1.39	1.39	1.31_5	1.31

p_1 : Specific polarization of solvent (tetrahydrofuran)
p_2 : Specific polarization of polymer
P_2 : Molecular polarization per monomer unit of polymer
μ : Dipole moment per monomer unit of polymer

$\alpha=\{(\varepsilon_{12}-\varepsilon_1)/w_2\}_{\mathrm{Av}}$, $\beta=\{(d_{12}-d_1)/w_2\}_{\mathrm{Av}}$

$[MR]_{\mathrm{D}}=14.11$ cc.

The dipole moments of stereospecific polymers were reported by Pohl et al. for isotactic and syndiotactic polymethyl methacrylates[12], by Krigbaum et al. for isotactic polystyrene in toluene[17], and recently by Imamura et al. for isotactic polyvinyl isobutyl ether[18].

The values reported in these papers are listed in Table IV. Isotactic polymers have larger moments than atactic polymers in all cases. With polymethyl methacrylates the values are of the order of iso. >atac. >syn. In this experiment the inverse tendency, syn. >atac., was observed with PVC.

Some of the theories shown above derived the formulae to express the values of the dipole moment per monomer unit of polar vinyl polymers, and concluded that generally the values for isotactic and syndiotactic chains are not the same. However, it can not be concluded either that isotactic polymers always have larger dipole moment values than syndiotactic polymers or the inverse. The formula should contain many factors in order to give an exact numerical value of the dipole moment.

Under the present circumstances, it is impossible to explain the inverse tendency obtained here.

However, it may be said that the stereospecificity of the chain can be related to the dipole moment value, and that it will be possible to determine the magnitude of the stereospecificity of the polar vinyl polymer through the measurement of the dipole moment.

TABLE IV. DIPOLE MOMENTS OF STEREOSPECIFIC POLYMERS

Polymer		Dipole moment D	Solvent	Temp. °C
Polystyrene[17]	isotactic	0.435	Toluene	38.4
	atactic	0.36	Toluene	38.4
Polymethyl methacrylate[12]				
	isotactic	1.43	Benzene	30
	atactic	1.35	Benzene	30
	syndiotactic	1.27	Benzene	30
Polyvinyl isobutyl ether[18]				
	isotactic	1.16	Benzene	25
	atactic	1.07	Benzene	25
Polyvinyl chloride				
Sample II,	atactic	1.31	Tetrahydrofuran	20
Sample I,	rich in syndiotactic	1.39	Tetrahydrofuran	20

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[17] W. R. Krigbaum and A. Roig, *J. Chem. Phys.*, **31**, 544 (1959).

[18] Y. Imamura, M. Takeda, S. Okamura and T. Higashimura, ibid., **33**, 631 (1960).

Effect of the Solvent on the Conformation of Polymer Molecules.—The dipole moment measurements so far mentioned were carried out with a polar solvent, tetrahydrofuran, because low-temperature polymerized PVC is insoluble in any nonpolar solvent. The effect of polar solvent should be discussed.

The total dipole moment of N-mer, μ_T, is expressed by

$$\langle \mu_T^2 \rangle / N = \mu^2 = \mu_0^2 \phi$$

where μ_0 is the moment of the individual dipole and ϕ is the interaction parameter.

Marchal and Benoit[19] explained that ϕ is independent of N when $N \rightarrow \infty$ under the conditions; (1) the dipole of each monomer unit is on a bisector of the valence angle of skeleton chain, and (2) the mean square end-to-end distance of the chain is proportional to N^α, where $\alpha < 2$.

The first condition can be easily modified: it is on the bisecting plane. Then both conditions seem to be satisfied by polyvinyl chloride. In such a case ϕ becomes the function only of the short-range conformations, such as valence angles, internal rotations etc., and long-range ones can be neglected.

Taking μ_0 to be the dipole moment of the reference substance close in the structure to the monomer unit, we can determine ϕ from the measurement of μ_0 and μ. In this way the solvent effect upon short-range conformation can be estimated.

Of course, the values of μ_0 and μ are affected by the choice of solvent, owing to the change in electrostatic interaction, but when the values of ϕ determined from μ_0 and μ in polar and nonpolar solvents coincide, one may assume that the short-range conformation of the molecules is not affected appreciably by the interaction between the solvent and polymer molecules.

Marchal et al. showed that the value of ϕ is almost independent of the polarity of solvents with polymethyl methacrylate[19,20]. In order to see if the same situation holds with PVC, *sec*-butyl chloride was selected as the reference substance; its dipole moment and that of commercial PVC were measured in dioxane and in tetrahydrofuran by the use of the same apparatus at the same temperatures as above. ϕ values were determined from the observed dipole moments and are listed in Table V.

TABLE V. INTERACTION BETWEEN POLYVINYL CHLORIDE AND SOLVENT

Temp. °C	Solvent	μ_0, D	μ, D	ϕ
20	Dioxane	2.12	1.61	0.59
20	Tetrahydrofuran	1.64	1.31_5	0.64
40	Dioxane	2.12	1.62	0.59
40	Tetrahydrofuran	1.66	1.31	0.62

μ : Dipole moment per monomer unit of PVC
μ_0 : Dipole moment of *sec*-butyl chloride

TABLE VI. INTERACTION BETWEEN POLYMETHYL METHACRYLATE AND SOLVENT[19,20]

Temp. °C	Solvent	μ_0^2	μ^2	ϕ	ϕ_{MB}
25	Benzene	2.99	1.87	0.62	—
25	Dioxane	2.96	1.82	0.61	0.65
25	Chloroform	1.98	1.22	0.61	0.62
25	Butyl acetate	0.34	0.20	0.60	0.58

μ : Dipole moment per monomer unit of polymethyl methacrylate
μ_0 : Dipole moment of methyl propionate

They proved to be 0.63 (tetrahydrofuran) and 0.59 (dioxane) and do not differ appreciably. The results reported by Marchal et al. with polymethyl methacrylate are listed in Table VI for purposes of reference, where ϕ_{MB} is the value of ϕ reported in the older report.

As in the case with polymethyl methacrylate, it can be said that the interaction between the molecules of the polymer and the solvent seems to have no significant effect on the short-range conformation of the PVC molecules in tetrahydrofuran and that the determination of the apparent dipole moment in polar solvent will serve for purposes of relative comparison.

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