Study on Dipole Moments of Macromolecules II. Dipole Moments of *p*-Methoxytoluene, *p*-Bromoethylbenzene and *p*-Bromotoluene as Structural Units of Poly(*p*-methoxystyrene) and Poly(*p*-bromostyrene)

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ABSTRACT: The dipole moments of *p*-methoxytoluene (*p*-MeOTol), *p*-bromoethylbenzene (*p*-BrEtBz), and *p*-bromotoluene (*p*-BrTol) corresponding to structural units of poly(*p*-methoxystyrene) and poly(*p*-bromostyrene) were determined from dielectric constant and density measurements on their benzene, *p*-dioxane, and toluene solutions over the temperature range of 25–55°C, and we examined the effects of solvent and temperature on the dipole moments. It was found that the observed dipole moment μ_0 is sensitive to the solvent and gives a larger value when the dielectric constant of solvent used for measurements is smaller. The dipole moments obtained for *p*-MeOTol at 25°C were 1.304 D in *p*-dioxane, 1.257 D in benzene and 1.204 D in toluene, and the μ_0 values of *p*-BrEtBz were 2.086 D in *p*-dioxane and 2.007 D in benzene. The results were interpreted on the basis of Higashi's theory. Temperature dependence of the dipole moments was also observed. The observed values of μ_0 obtained for *p*-MeOTol and *p*-BrEtBz and *p*-BrTol slightly increased with increasing temperature, which is explainable as due to the change of dielectric constant of solvent with temperature.

KEY WORDS Dipole Moment / Dielectric Constant / *p*-Methoxytoluene / *p*-Bromoethylbenzene / *p*-Bromotoluene / Solvent Effect /

In the preceding paper,¹ we reported the dielectric measurements of organic solvents, and poly(*p*-methoxystyrene) in solution, introducing a new apparatus consisting of capacitance bridge and a three-terminal platinum electrodes cell. The dielectric constants obtained using the new apparatus were accurate and the accuracy of the dipole moment was improved by one more order than that obtained before.^{2,3}

The mean square dipole moment of polymer is a configuration-dependent property of the polymer chain when the polymer has polar groups in each structural unit. The dipole moment ratio, given by the equation $D_r = \langle m^2 \rangle / x\mu_0^2$, is an analogue of the characteristic ratio, $C_r = \langle r_0^2 \rangle / nl^2$, of the chain dimension, where $\langle m^2 \rangle$ is the mean square dipole moment

of the polymer chain with x bond dipoles in magnitude μ_0 in the chain and $\langle r_0^2 \rangle$ is the mean square end-to-end distance of the unperturbed chain with n bonds of length l , and an important parameter often used in conformational analysis of polymer chains.

A number of experimental results of the dipole moments of polymers determined in various solvents and temperatures have been reported but in the estimation of D_r , a fixed value of μ_0 has generally been used, assuming that solvent and temperature have little effect on the value of μ_0 . However, as an earlier study⁴ showed, the dipole moments of organic compounds, such as chlorobenzene, nitrobenzene, and ethyl ether were sensitive to the solvent in which the measurements were performed, and theoretical studies of solvent

effect on μ_0 were reported by Higashi⁴ and others.⁵⁻⁷ The Experimental accuracy of dielectric measurements was not very high at earlier time and it was rather difficult to verify solvent effect on μ_0 , but lately an accuracy of estimating the dipole moment has been much improved and it will be significant to determine accurately μ_0 in each solvent and at the same temperature as for polymers in order to get more exact values of the dipole moment ratio.

In this study, the dipole moments of *p*-methoxytoluene, *p*-bromoethylbenzene, and *p*-bromotoluene which were chosen as the model compounds of structural units of poly(*p*-methoxystyrene) (PMeOSt) and poly(*p*-bromostyrene) (PBrSt), were determined in benzene, *p*-dioxane, and toluene over the temperature range between 25 and 55°C, and we examined their dependence on solvent and temperature.

EXPERIMENTAL

Materials

p-Methoxytoluene (*p*-MeOTol) and *p*-bromotoluene (*p*-BrTol) were from Tokyo Kasei Co., Ltd. and *p*-bromoethylbenzene (*p*-BrEtBz) was from Aldrich Chemical Co. These materials were repeatedly purified by distillation. Just before each distillation, these materials were dried by passage through a molecular sieve 4A.

p-Dioxane, benzene, and toluene as the solvents were dried by repeated passage through the molecular sieve 4A and distilled before use.

Measurements of Dielectric Constant and Density

The dielectric constants were measured with a capacitance bridge mounted on a three-terminal platinum electrodes cell, at a frequency of 10 kHz. The cell is composed of a double-walled Pyrex glass tube and requires *ca.* 70 cm³ of solution. The cell capacitance with air is $C_0 = 38.3203 \pm 0.0007$ pF at 25°C.

Temperature was controlled within $\pm 0.01^\circ\text{C}$. The concentrations of solutions were in the range of 1 to 3 weight percent.

Densities were determined by the "flask-type" pycnometer with volume of *ca.* 10 cm³.

RESULTS AND DISCUSSION

Dipole moment was estimated according to the conventional method⁸ by measuring the dielectric constant and density of solutions. The specific polarization, p_2 , of the solute at infinite dilution was calculated according to Halverstadt-Kumler equations⁹

$$p_2 = p_1 \left\{ 1 + \frac{3\alpha}{(\epsilon_1 - 1)(\epsilon_1 + 2)} - \frac{\beta}{\rho_1} \right\} \quad (1)$$

$$p_1 = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{\rho_1}$$

$$\alpha = \frac{d(\epsilon_{12} - \epsilon_1)}{dw} \quad (2)$$

$$\beta = \frac{d(\rho_{12} - \rho_1)}{dw} \quad (3)$$

where, w is the weight fraction of solute, ϵ , the dielectric constant, ρ , density, and subscripts 1, 2, and 12 refer to solvent, solute and solution, respectively.

According to Debye's theory,⁸ the molecular polarization of a solute P_2 ($= p_2 \cdot M$, M , the molecular weight of solute) is given as:

$$P_2 = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho} = \frac{4\pi N}{3} \left(\gamma + \frac{\mu^2}{3kT} \right) \quad (4)$$

$$P_2 = P_0 + P_E + P_A$$

$$P_0 = \frac{4\pi N}{9kT} \mu^2, \quad P_E + P_A = \frac{4\pi N}{3} \gamma$$

where, γ is the polarizability, P_0 , P_E , and P_A are the orientation, electronic, and atomic polarizations, respectively, k is the Boltzmann's constant, N , Avogadro's number and T , temperature.

The dipole moment is then calculated by the

Table I. Dielectric constants and densities of *p*-dioxane, benzene, and toluene

Temp	<i>p</i> -Dioxane		Benzene		Toluene	
°C	ϵ_1	$\rho_1/\text{g cm}^{-3}$	ϵ_1	$\rho_1/\text{g cm}^{-3}$	ϵ_1	$\rho_1/\text{g cm}^{-3}$
25	2.2061	1.02807	2.2742	0.87362	2.3762	0.86209
30	2.1978	1.02245	2.2643	0.86828	2.3650	0.85744
35	2.1895	1.01683	2.2544	0.86294	2.3537	0.85278
40	2.1813	1.01121	2.2445	0.85760	2.3425	0.84813
45	2.1730	1.00559	2.2346	0.85227	2.3313	0.84348
50	2.1648	0.99996	2.2247	0.84693	2.3201	0.83882
55	2.1565	0.99434	2.2148	0.84159	2.3089	0.83417

following equation:

$$\mu = [(9kT/4\pi N)\{P_2 - (P_E + P_A)\}]^{1/2} \\ = 0.01281[P_2 - (P_E + P_A)T]^{1/2} \quad (5)$$

The molecular refraction for the D-line $[\text{MR}]_D$ is taken as the sum of P_E and P_A :

$$P_E + P_A = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{\rho} = [\text{MR}]_D \quad (6)$$

where n_D is the refractive index of the solute for the D-line. The value of $[\text{MR}]_D$ was calculated as the sum of appropriate atomic refractions of the constituent atoms. The values of $[\text{MR}]_D$ for *p*-MeOTol, *p*-BrEtBz, and *p*-BrTol were obtained as 37.186 cm³, 43.308 cm³, and 38.690 cm³, respectively.

The dielectric constants and densities of the solvents are listed in Table I. The specific increments α and β at infinite dilution were obtained from the slopes of the linear relationships of ϵ_{12} vs. w and ρ_{12} vs. w plots, respectively. A typical example is shown in Figure 1, in which the resulting lines were located by least-squares analysis.

The results of dielectric measurements of *p*-MeOTol, *p*-BrEtBz, and *p*-BrTol obtained in three solvents over the temperature range of 25–55°C are given in Tables II and III. In Figures 2 and 3, the dipole moments of *p*-MeOTol and *p*-BrEtBz are plotted against temperature. The results show that the μ_0 values are sensitive to the solvent in which the

dielectric measurements are performed. The μ_0 values obtained at 25°C for *p*-MeOTol were 1.304 D (in *p*-dioxane) and 1.257 D (in benzene) and 1.204 D (in toluene), and those for *p*-BrEtBz were 2.086 D (in *p*-dioxane) and 2.007 D (in benzene). The difference between the values obtained in different solvents was small but beyond the range of the experimental error, since in the present study, the measurements of ϵ and ρ were very accurate and experimental uncertainty in μ_0 is considered to be less than 1%. The experimental results indicate that the μ_0 values depend on the solvent used for the measurements.

In the dielectric measurements of a polar solute in nonpolar solvent, it was pointed out⁵ that the polarization of the nonpolar solvent molecules is affected by the presence of polar solute molecules and some dipole moments are induced in solvent molecules. The moments induced in the solvent molecules induce moments in the solute molecules, this causing μ_0 in solution differ from that in the vapor state (μ_{gas}).

Müller *et al.*,¹⁰ treated this subject in the past and showed that dipole moments measured in solution (μ_{sol}) were different from those measured in the vapor state (μ_{gas}). This is the so-called solvent effect. Followed by Müller's paper, several theoretical studies^{4,6,7} on solvent effects were made. According to the theories, the dipole moment in solution (μ_{sol}) depends on the dielectric constant of the

Figure 1. Plots of ϵ_{12} versus w and ρ_{12} versus w for *p*-methoxytoluene in benzene solution at the temperature indicated. w , weight fraction of solute; ϵ , dielectric constant; ρ , density; 12 refers to solution.

solvent. Higashi⁴ treated the solvent effect by considering the shape effect of the solute molecules and derived the following relation:

$$\frac{\mu_{\text{sol}}}{\mu_{\text{gas}}} = 1 + 3 \frac{\epsilon_1 - 1}{\epsilon_1 + 2} A \quad (7)$$

Table IIa. Temperature dependence of the dipole moment for *p*-MeOTol in *p*-dioxane

Temp	α	β	p_2	P_2	μ_0
°C		g cm^{-3}	$\text{cm}^3 \text{g}^{-1}$	$\text{cm}^3 \text{mol}^{-1}$	debye
25	1.7805	-0.05913	0.58864	71.912	1.303 ₉
30	1.7432	-0.06054	0.58586	71.572	1.308 ₃
35	1.7060	-0.06195	0.58300	71.223	1.312 ₃
40	1.6687	-0.06335	0.58006	70.864	1.315 ₉
45	1.6315	-0.06476	0.57704	70.495	1.319 ₁
50	1.5943	-0.06617	0.57394	70.116	1.321 ₈
55	1.5570	-0.06757	0.57074	69.726	1.324 ₁

Table IIb. Temperature dependence of the dipole moment for *p*-MeOTol in benzene

Temp	α	β	p_2	P_2	μ_0
°C		g cm^{-3}	$\text{cm}^3 \text{g}^{-1}$	$\text{cm}^3 \text{mol}^{-1}$	debye
25	1.3904	0.08740	0.56842	69.441	1.256 ₆
30	1.3610	0.08800	0.56543	69.077	1.259 ₉
35	1.3317	0.08860	0.56236	69.701	1.262 ₈
40	1.3023	0.08920	0.55919	68.314	1.265 ₁
45	1.2730	0.08980	0.55594	67.917	1.267 ₀
50	1.2436	0.09043	0.55257	67.505	1.268 ₄
55	1.2143	0.09103	0.54912	67.084	1.269 ₂

Table IIc. Temperature dependence of the dipole moment for *p*-MeOTol in toluene

Temp	α	β	p_2	P_2	μ_0
°C		g cm^{-3}	$\text{cm}^3 \text{g}^{-1}$	$\text{cm}^3 \text{mol}^{-1}$	debye
25	1.2383	0.10167	0.54676	66.796	1.204 ₀
30	1.2140	0.10143	0.54450	66.519	1.208 ₄
35	1.1898	0.10118	0.54217	66.235	1.212 ₃
40	1.1656	0.10094	0.53977	66.941	1.216 ₀
45	1.1413	0.10070	0.53729	66.638	1.219 ₁
50	1.1171	0.10045	0.53473	66.326	1.221 ₉
55	1.0926	0.10020	0.53205	65.998	1.224 ₂

where A is a constant depending on the molecular shape of the solute and location of the dipole in the molecule. When a solute molecule is spherical, having a dipole at its center, A is zero, and then $\mu_{\text{sol}} = \mu_{\text{gas}}$, i.e., the solvent effect vanishes. When a solute molecule is an ellipsoid of rotation and the dipole is

Table IIIa. Temperature dependence of the dipole moment for *p*-BrEtBz in *p*-dioxane

Temp °C	α	β g cm ⁻³	p_2 cm ³ g ⁻¹	P_2 cm ³ mol ⁻¹	μ_0 debye
25	3.0115	0.22660	0.71418	132.168	2.085 ₇
30	2.9513	0.22859	0.70809	131.041	2.089 ₈
35	2.8910	0.23166	0.70157	129.835	2.092 ₄
40	2.8308	0.23258	0.69549	128.710	2.095 ₅
45	2.7705	0.23457	0.68897	127.503	2.097 ₂
50	2.7103	0.23656	0.68230	126.269	2.098 ₁
55	2.6501	0.23856	0.67549	125.007	2.098 ₁

Table IIIb. Temperature dependence of the dipole moment for *p*-BrEtBz in benzene

Temp °C	α	β g cm ⁻³	p_2 cm ³ g ⁻¹	P_2 cm ³ mol ⁻¹	μ_0 debye
25	2.4307	0.30579	0.67866	125.595	2.007 ₁
30	2.3800	0.30518	0.67363	124.665	2.012 ₄
35	2.3294	0.30453	0.66848	123.712	2.017 ₀
40	2.2787	0.30391	0.66317	122.729	2.020 ₈
45	2.2280	0.30330	0.65771	121.717	2.023 ₉
50	2.1773	0.30265	0.65210	120.680	2.026 ₂
55	2.1266	0.30203	0.64632	119.610	2.027 ₆

Table IIIc. Temperature dependence of the dipole moment for *p*-BrTol in benzene

Temp °C	α	β g cm ⁻³	p_2 cm ³ g ⁻¹	P_2 cm ³ mol ⁻¹	μ_0 debye
25	2.4999	0.34127	0.67786	115.939	1.944 ₇
30	2.4474	0.33932	0.67305	115.115	1.950 ₄
35	2.3949	0.33738	0.66809	114.267	1.955 ₅
40	2.3423	0.33540	0.66300	113.397	1.959 ₉
45	2.2898	0.33349	0.65774	112.497	1.963 ₆
50	2.2373	0.33151	0.65234	111.574	1.966 ₅
55	2.1848	0.32956	0.64678	110.622	1.968 ₇

directed to the longer axis of the ellipsoid, $A < 0$, i.e., $\mu_{\text{sol}} < \mu_{\text{gas}}$, and the dipole moment decreases with increasing dielectric constant. For an ellipsoid molecule with the dipole directed along the shorter axis of the molecule, $A > 0$, i.e., $\mu_{\text{sol}} > \mu_{\text{gas}}$, and the dipole moment increases with increase of dielectric constant.

Figure 2. Temperature dependence of the dipole moments for *p*-methoxytoluene measured in *p*-dioxane, benzene, and toluene solutions. D, *p*-dioxane; B, benzene; T, toluene. **Figure 3.** Temperature dependence of the dipole moments for *p*-bromoethylbenzene measured in *p*-dioxane and benzene solutions. D, *p*-dioxane; B, benzene.

Both *p*-MeOTol and *p*-BrEtBz are regarded as ellipsoidal molecules with the dipole directed along the longer axis of the molecule.

According to the Higashi's theory, the dipole moments of these molecules in solution should decrease with increase of dielectric constant of the solvent. The dielectric constants of the solvents obtained at 25°C are as follows, 2.2061 (*p*-dioxane), 2.2742 (benzene), and 2.3762 (toluene) as shown in Table I. As mentioned above, μ_0 of *p*-BrEtBz in *p*-dioxane is larger than that in benzene and the dipole moment of *p*-MeOTol decreases in the order of the solvent, *p*-dioxane, benzene, and toluene. These results are consistent with Higashi's theory.

Concerning temperature dependence of dipole moment, it was observed that the values of μ_0 slightly increased with increase of temperature but not linearly. The changes of μ_0 with temperature were very little compared to those with solvent, but the observed values for *p*-MeOTol, *p*-BrEtBz, and *p*-BrTol consistently increased with temperature.

There are few studies on temperature dependence of the dipole moments for organic compounds corresponding to polymer structural units. Guest and Stockmayer *et al.*¹¹ investigated the influence of temperature on the dipole moment of methyl *tert*-butyl ketone as a model compound for the structural unit of poly(*tert*-butyl vinyl ketone). They obtained values of μ_0 as 2.75 D (15°C), 2.76 D (25°C), 2.77 D (35°C), 2.76 D (45°C), and 2.76 D (55°C), and concluded that the dipole moment is independent of temperature. Recently, Riande and Saiz *et al.*¹² reported that the dipole moments of phenyl propionate and *p*-chlorophenyl propionate in benzene, which are structural unit compounds of poly(phenyl acrylate) and poly(*p*-chlorophenyl acrylate), respectively, showed positive temperature coefficients; *i.e.*, they increased with increasing temperature. These results were interpreted in terms of the change of bond angles about C–O–Ph bonds of ester groups with temperature.

The intramolecular rotation in the molecules of *p*-MeOTol and *p*-BrEtBz will change with temperature, but this does not affect the values

of their dipole moments as a whole. As seen in Table I, the dielectric constants of *p*-dioxane, benzene, and toluene, which were used for measurements of this study, decreased with increase of temperature. As already described, according to the theories by Higashi⁴ and others,^{5–7} the dipole moment determined in solution gives greater values when the solvent used for measurement has a smaller value of the dielectric constant. Accordingly, the temperature dependence of the dipole moments observed in this study could be interpreted as due to change of dielectric constant of the solvent with temperature.

There are two procedures generally accepted for an evaluation of the dipole moment of polymers in solution. One is to evaluate the dipole moment from dielectric constants and densities of the polymer solution by using the equations of Halverstadt–Kumler and Debye, and the other is the Guggenheim–Smith method,¹³ using dielectric constants and the refractive index of the polymer solution. In the preceding paper, we examined these two methods for estimation of the dipole moment of PMeOSt in benzene solution. The results of the dipole moment obtained by the two methods were not identical but the discrepancy was insignificant.

The dipole moments of polymers such as PMeOSt and PBrSt are expected to be independent of chain expansion due to long-range interactions.^{14–18} Accordingly, the dipole moments of such polymers should give the same value even if measured in any nonpolar solvent. However, from the results of this study, it is expected that the dipole moments of such polymers in solution depend on the dielectric constant of solvent. Moreover, the change of the dipole moment with temperature reflects not only conformational change of the polymer chain, but also change of dielectric constant of solvent with temperature.

This suggests that in the calculation of the dipole moment ratio, $D_r = \langle m^2 \rangle / x\mu_0^2$, μ_0 values

determined in the same conditions, both temperature and solvent species, as for the polymer, should be used.

The dipole moment ratio of PMeOS_t and PBrSt will be discussed using the results of this study in a subsequent paper.¹⁹

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