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Dipole Moment and Molecular Structure of Copolymers. III. Dipole Moment of *p*-Methoxystyrene - Styrene Copolymers and *p*-Chlorostyrene - Styrene Copolymers

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The *p*-methoxystyrene monomer has been synthesized from anisole through *p*-methoxyacetophenone and *p*-methoxyphenyl methyl carbinol. Then copolymers of *p*-methoxystyrene and styrene have been prepared. The dielectric properties of the copolymers in a benzene solution have been measured, and it has been found that the value of the dipole moment, μ, of the *p*-methoxystyrene monomer unit in the copolymers increases with an increase in the styrene content, e. g., from 1.21 D (for poly-*p*-methoxystyrene) to 1.32 D (for the copolymer in which the mole fraction of *p*-methoxystyrene is 0.175) at 20°C. The variation in the value of μ has been discussed in view of the detailed arrangement of polar monomer units. The theory concenring the relation between the dielectric polarization and the detailed structure of the copolymer molecule developed in the preceding paper, Part I, has been applied to the experimental results. In addition, a similar analysis has been made for the dielectric polarizations of the *p*-chlorostyrene - styrene copolymers which had been measured previously by one of the authors.

The properties of copolymers should depend on the detailed arrangement of the monomer units as well as on their composition. For instance, there are three different arrangements that can be considered for a copolymer which contains equimoles of A and B monomer units:

(1) —AAAAAABBBBBBAAAAABBBBB—

(2) —ABABABABABABABABABABAB—

(3) —AABBBAAABABAABBBABBAAA—

(1) The block arrangement, in which long sequences predominate. A copolymer having this structure is usually called a block copolymer.

(2) The regular alternating arrangement, in which the sequence length is always 1.

(3) The random arrangement, in which short sequences of A units alternate with short sequences of B units in an essentially random fashion. This arrangement may be considered the molecular structure of a normal copolymer.

The copolymers with these three structures can be expected to have different properties: they may be considered to be different chemical species, even though they have the same overall composition. The copolymer which has a structure of type 1 might be expected to resemble, in many respects, a simple mixture of the homopolymers of A and B. A short-sequence copolymer, on the other hand, would be expected to be unlike a mixture of the two homopolymers.

The reaction mechanism of copolymerization has been discussed in detail more than once.[1,2] From the basic theory of copolymerization, it is possible to calculate the number-average sequence length of monomer units and, hence, a statistically probable arrangement of individual monomer units in the copolymer molecular chain, the monomer reactivity ratios of which are known. However, as has already been mentioned,[3,4] there has yet been no convincing experimental evidence of the distribution of sequence lengths of individual monomer units in the copolymer molecule. A number of methods have been proposed in attempts to gain information about the detailed arrangement of individual monomer units in copolymers. They include the dechlorination of the vinyl chloride - vinyl acetate copolymer with zinc by Marvel et al.,[5] the intramolecular gamma-lactone formation in vinyl alcohol - acrylic acid copolymers,[6] and a study of the solution properties of partially-acetylated polyvinyl alcohol.[7] Recently developed methods have include the study of the dielectric properties of *p*-chlorostyrene-styrene copolymers in the solid state[8] and the

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[1] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[2] T. Alfrey, Jr., J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York (1952).

[3] M. Shima, *J. Polymer Sci.*, **56**, 213 (1962).

[4] M. Shima and A. Kotera, *Makromol. Chem.*, **64**, 172 (1963).

[5] C. S. Mervel, G. D. Jones, T. W. Mastin and G. L. Schertz, *J. Am. Chem. Soc.*, **64**, 2358 (1942).

[6] T. Matsumoto, *Kobunshi Kagaku*, **7**, 142 (1950); I. Sakurada and K. Kawasaki, ibid., **8**, 142 (1951).

[7] I. Sakurada and O. Yoshizaki, ibid., **10**, 306 (1953); H. Matsuda, K. Naraoka, S. Ishiguro and A. Kotera, ibid., **12**, 10 (1955).

[8] R. N. Work and Y. M. Trehu, *J. Appl. Phys.*, **27**, 1003 (1956).

TABLE I. DIELECTRIC POLARIZATION AND DIPOLE MOMENTS OF *p*-METHOXYSTYRENE MONOMER UNIT IN *p*-METHOXYSTYRENE - STYRENE COPOLYMERS

Temp., °C	x*[a]	α	β	p_2	P_{Av}, cc.	μ, Debye	P_{Calc}, cc.
20	1.0000	1.407	−0.268	0.5223	70.1	1.21	
	0.8347	1.289	−0.274	0.5388	71.2	1.23	71.2
	0.5799	1.026	−0.251	0.4991	72.8	1.26	73.0
	0.4075	0.839	−0.237	0.4259	74.5	1.29	74.3
	0.1749	0.554	−0.222	0.3772	76.0	1.32	76.1
	(0.0000*[b]	0.323	−0.213	0.3370	35.1	0.28)	
50	1.0000	1.309	−0.310	0.5123	68.8	1.24	
	0.8347	1.147	−0.303	0.4901	69.9	1.26	69.6
	0.5799	0.952	−0.289	0.4478	70.9	1.28	71.1
	0.4075	0.789	−0.277	0.4185	72.2	1.31	72.2
	0.1749	0.529	−0.254	0.3738	73.8	1.34	73.7
	(0.0000*[b]	0.343	−0.255	0.3364	35.0	0.29)	

*a x is the mole fraction of *p*-methoxystyrene in the copolymer. $\alpha=\left(\frac{\varepsilon_{12}-\varepsilon_1}{w_2}\right)$ and $\beta=\left(\frac{v_{12}-v_1}{w_2}\right)$ where ε is the dielectric constants, and v is the specific volume. The suffixes 1, 2, and 12 refer to solvent (benzene), solute (copolymer), and solution. p_2 is the specific polarization of the copolymer. P_{Av} is the average molecular polarization of a *p*-methoxystyrene unit in the copolymer molecule. μ is the dipole moment calculated from the equation

$$\mu = 0.0128 \times [\{P_{Av} - (\mathrm{MR})_{\mathrm{D}}\} T]^{1/2}$$

in which 39.7 cc. was used as the value of $(\mathrm{MR})_{\mathrm{D}}$ for the *p*-methoxystyrene monomer unit.

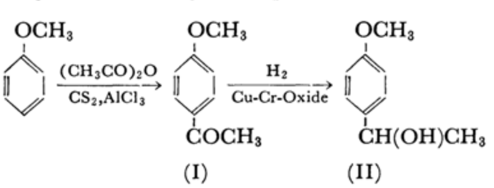
*b Polystyrene

infrared spectroscopic study of acrolein-acrylonitrile copolymers.[9] One of the present authors previously measured the dielectric properties of copolymers of methyl methacrylate - styrene[3] and methyl acrylate - styrene[4] in benzene solution, and developed a theory which connects the average dielectric polarization of copolymers with the detailed arrangement of monomer units in the copolymer molecule.

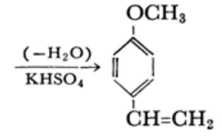
In this paper, we will work on the dielectric properties of copolymers of *p*-methoxystyrene and styrene, and will discuss the experimental results by applying the theory described in a preceding paper, Part I.[3] In addition, we will describe the results of a similar analysis for the *p*-chlorostyrene - styrene copolymers, the dielectric polarizations of which were measured previously by one of the present authors.[10]

Experimental

The Synthesis of the *p*-Methoxystyrene Monomer.—The *p*-methoxystyrene monomer was synthesized through the following three processes:



(I) (II)



(III)

p-Methoxyacetophenone (I) was prepared, by means of the Friedel-Craft reaction, from anisole and acetic acid anhydride in carbon disulfide, in the presence of anhydrous aluminum chloride.[11] *p*-Methoxyphenyl methyl carbinol (II) was obtained by the reduction of *p*-methoxyacetophenone with copper-chromium-oxide and hydrogen; this was carried out in an autoclave under a high pressure of more than 100 atm.[12,13] The reaction of the dehydration was carried out by heating *p*-methoxyphenyl methyl carbinol with acid potassium sulfate, and then distilling the *p*-methoxystyrene.

Copolymerization.—The *p*-methoxystyrene monomer was dried with anhydrous sodium sulfate and distilled three times under reduced pressure prior to polymerization; the b. p. was 84—86°C/8 mmHg. The styrene monomer used in these experiments was a commercial one, which was washed with a 10% aqueous solution of sodium hydroxide and water, dried with anhydrous sodium sulfate, and distilled under reduced pressure; the b. p. was 45—46°C/17 mmHg.

Monomer mixtures which total about 25 g. and which contain no catalyst were prepared over a whole range of composition and sealed in glass tubes. The polymerizations were carried out thermally by holding the tubes in an oil-bath at 100°C for about 120 hr. The

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[9] R. C. Schultz, H. Cherdon and W. Kern, *Makromol. Chem.*, **29**, 190 (1959).

[10] A. Kotera, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **63**, 364 (1942).

[11] "Organic Syntheses," 1, 109; C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **46**, 1889 (1937).

[12] J. H. Brown and C. R. Marvel, ibid., **59**, 1176 (1937).

[13] H. Adkins, "Reaction of Hydrogen with Organic Compounds over Copper-Chromium-Oxide and Nickel Catalysts," Japanese translation, Kawaide Shobō, Tokyo (1937).

polymers were precipitated from a benzene solution into methanol and dried in a high vacuum.

Measurements of the Dielectric Polarization of Copolymers.—The experimental determination of the dielectric polarization of copolymers was carried out in the usual way by measuring the dielectric constants and the specific volumes of the copolymer solutions. The apparatus was similar to that described in Part I.[3] The cell is composed of three concentric platinum cylinders in a glass tube, and its capacity is about 35 $\mu\mu$F. The cell capacitance measurements were made by the heterodyne-beat method at a frequency of 500 kilocycles per second. The specific volumes were measured by "the mess-flask type" pycnometer, the volume of which was about 10 cc. The extrapolated values of the specific polarization of the copolymer at an infinite dilution were calculated according to the Halverstadt-Kumler equation[14]:

$$p_2=\frac{3\alpha v_1}{\varepsilon_1+2}+(v_1+\beta)\frac{\varepsilon_1-1}{\varepsilon_1+2} \qquad (1)$$

where ε_1 and v_1 are the dielectric constant and the specific volume of the solvent (benzene) respectively. α and β, denoting the dielectric constant and the specific volume of solution, ε_{12} and v_{12} respectively, are given as:

$$\varepsilon_{12}=\varepsilon_1+\alpha w_2, \qquad v_{12}=v_1+\beta w_2$$

where w_2 is the weight fraction of the solute (the copolymer).

The dielectric constants and the specific volumes were measured on four solutions of different concentrations, from 1% to 9%, for each copolymer sample. The values of α and β obtained are given in Table I.

The specific polarization of copolymer, p_2, can be expressed as follows:

$$p_2=w_{\mathrm{A}}p_{\mathrm{MeO}}+(1-w_{\mathrm{A}})p_{\mathrm{St}} \qquad (2)$$

where w_{A} is the weight fraction of *p*-methoxystyrene in the copolymer, and p_{MeO} and p_{St} are the effective specific polarizations associated with *p*-methoxystyrene and styrene monomer units, respectively, in the copolymer molecule. As the styrene monomer is nonpolar, the value of p_{St} may not be very greatly influenced by the neighboring groups. Therefore, it was assumed that the value of p_{St} is the same as that of polystyrene. The average molecular polarization of *p*-methoxystyrene monomer units in the copolymer molecule, $P_{Av}(=M_{\mathrm{A}}p_{\mathrm{MeO}}$: M_{A} is the molecular weight of the *p*-methoxystyrene monomer unit) was calculated from Eq. 2. Further, the sum of electronic polarization and atomic polarization was assumed to be equal to the molecular refraction for the D line calculated from the atomic refractions of the constituent atoms. The dipole moment of the *p*-methoxystyrene unit was calculated by the equation:

$$\mu=0.0128\times\{(P_{Av}-[\mathrm{MR}]_{\mathrm{D}})T\}^{1/2} \qquad (3)$$

$[\mathrm{MR}]_{\mathrm{D}}$; the molecular refraction for the D line.

Results and Discussion

Experimental Results for *p*-Methoxystyrene-Styrene Copolymers.—The results of experiments are summarized in Table I. The tendency found in the cases of the copolymers of methyl methacrylate-styrene and methyl acrylate-styrene is also observed in the variation in μ value with the composition of the copolymers. The value of the effective dipole moment of the *p*-methoxystyrene monomer unit in the copolymers increased with an increase in the styrene content; i. e., the value of μ increased from 1.21 D for poly *p*-methoxystyrene ($x=1.000$) to 1.32 D for the copolymer of $x=0.1749$ at 20°C and from 1.24 D to 1.34 D at 50°C. This may be interpreted qualitatively as follows: the value of the dipole moment of the *p*-methoxystyrene monomer unit obtained from the measurement of the homopolymer is not the value of the isolated unit. Rather, it includes the effect of intramolecular interactions between the neighboring polar units along the chain, i. e., the influence of dipole-dipole interactions, steric hindrance, and so on. Because of the influence of these interactions, the value of μ in the poly-*p*-methoxystyrene should be smaller than that of the isolated equivalent unit. In the copolymer molecule, the influence of the dipole-dipole interactions may be reduced by the nonpolar styrene units separating the polar units. The increase in the styrene content should increase the isolated *p*-methoxystyrene units in the copolymer molecule, and, accordingly, the value of μ will approach that of the isolated unit.

The Relation between the Dielectric Polarization and a Detailed Arrangement of Polar Monomer Units in the Copolymer Molecule.—By applying the theory described in Part I,[3] to the experimental results, we shall attempt to treat quantitatively the relation between the dielectric polarization and the detailed arrangement of *p*-methoxystyrene units in the copolymer molecule. If it is assumed that the polar monomer units in a polar (A)-nonpolar (B) copolymer molecule can be classified into three types:

(1) two neighbors along the chain are the same polar units, A and A:

∼ A Ⓐ A ∼

(2) one neighbor is the polar unit A, and the other is the nonpolar unit B:

∼ A Ⓐ B ∼

(3) both neighbors are nonpolar units, B and B:

∼ B Ⓐ B ∼

and that these three types have different values of molecular polarization, P_{AA}, P_{AB} and P_{BB} respectively, then the average molecular polarization of the monomer unit, A, in the copolymer molecule, P_{Av}, may be given by the equation:

$$P_{Av}=P_{\mathrm{AA}}F_{\mathrm{AA}}+P_{\mathrm{AB}}F_{\mathrm{AB}}+P_{\mathrm{BB}}F_{\mathrm{BB}} \qquad (4)$$

where F_{AA}, F_{AB} and F_{BB} are the fractions of the polar monomer units A in the states of (1), (2) and (3) respectively. This equation can be transformed as follows, provided that f_{AA} is the

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[14] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

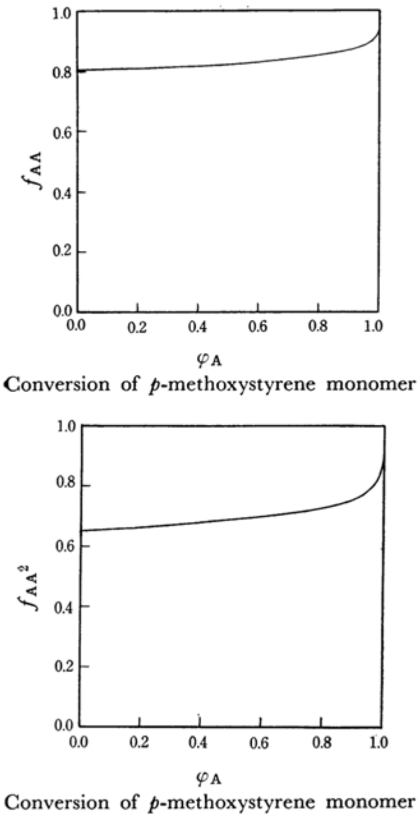

Fig. 1. Up, probability of AA sequence arising in copolymer; under, probability of double AA sequence arising in copolymer. $x_0=0.8347$

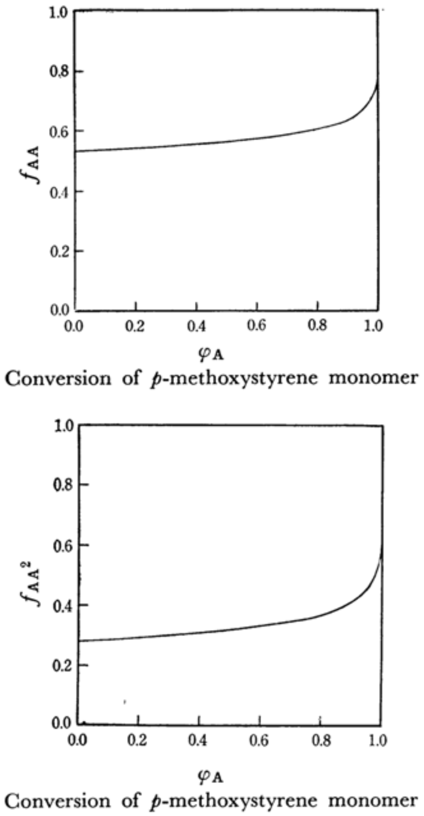

Fig. 2. Up, probability of AA sequence arising in copolymer; under, probability of double AA sequence arising in copolymer. $x_0=0.5799$

probability that a neighbor of the polar monomer unit A is polar:

$$P_{Av}=P_{AA}\overline{f_{AA}{}^2}+2P_{AB}(\overline{f_{AA}}-\overline{f_{AA}{}^2})+P_{BB}(1-2\overline{f_{AA}}+\overline{f_{AA}{}^2}) \quad (5)$$

The averages of f_{AA} and $f_{AA}{}^2$ can be calculated from the equations:

$$\overline{f_{AA}}=\frac{\int_0^{\varphi_A} f_{AA}\mathrm{d}\varphi_A}{\int_0^{\varphi_A}\mathrm{d}\varphi_A} \text{ and } \overline{f_{AA}{}^2}=\frac{\int_0^{\varphi_A} f_{AA}{}^2\mathrm{d}\varphi_A}{\int_0^{\varphi_A}\mathrm{d}\varphi_A} \quad (6)$$

where φ_A is the conversion of the monomer A. f_{AA} and φ_A are related to each other through the mole fraction, x, of the A monomer in the monomer mixture, as is given by the equations:[1]

$$f_{AA}=\frac{r_1x}{r_1x+1-x} \qquad \text{and}$$

$$(1-\varphi_A)=\left(\frac{x}{x_0}\right)^{1/(1-r_2)}\left(\frac{1-x}{1-x_0}\right)^{r_1/(1-r_1)}\times\left\{\frac{(r_1+r_2-2)x-(r_2-1)}{(r_1+r_2-2)x_0-(r_2-1)}\right\}^{r_1r_2-1/(1-r_1)(1-r_2)}$$

where x_0 is the x of the initial monomer mixture, and r_1 and r_2 are the monomer reactivity ratios. As f_{AA} and $f_{AA}{}^2$ can not be expressed as an explicit function of φ_A, we calculated the values of $\overline{f_{AA}}$ and $\overline{f_{AA}{}^2}$ by the numerical integrations of Eq. 6.

The Results of Calculation for Copolymers of *p*-Methoxystyrene - Styrene and *p*-Chlorostyrene - Styrene.—Figures 1—4 show f_{AA} and $f_{AA}{}^2$ as functions of the conversion, φ_A, of the A monomer for each sample of p-methoxystyrene - styrene copolymers. In this experiment, the monomers A and B referred to p-methoxystyrene and styrene respectively, and the values of $r_1=0.82$ and $r_2=1.16$[15] were employed in the calculation of f_{AA}. The values of $\overline{f_{AA}}$ and $\overline{f_{AA}{}^2}$ were obtained from the evaluation of the areas under the curves in these figures: they are given in Table III.

One of the present authors previously measured the dielectric properties of p-chlorostyrene - styrene copolymers in a benzene solution. Table II gives the results of these measurements.[16] We

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[15] C. Walling, E. R. Briggs, K. B. Wolfstein and F. R. Mayo, ibid., **70**, 1537 (1948).

[16] A. Kotera, *Kobunshi Kagaku*, **1**, 1 (1949).

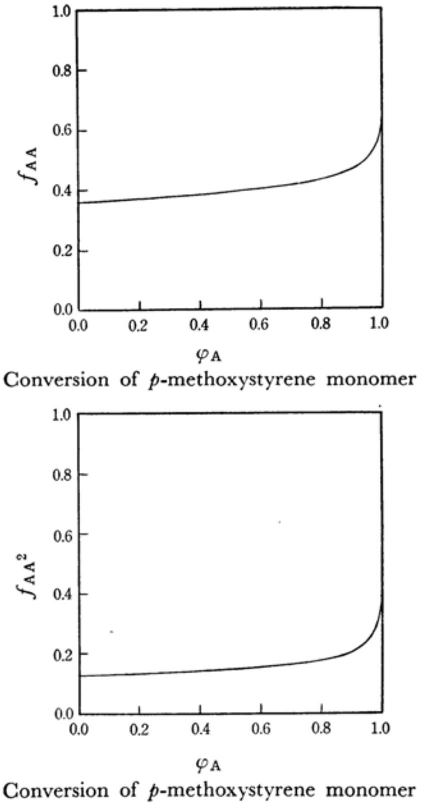

Fig. 3. Up, probability of AA sequence arising in copolymer; under, probability of double AA sequence arising in copolymer. $x_0=0.4075$

TABLE II. DIELECTRIC POLARIZATIONS AND DIPOLE MOMENT OF *p*-CHLOROSTYRENE MONOMER UNIT IN *p*-CHLOROSTYRENE - STYRENE COPOLYMERS

Temp. °C	w_A*a	p_2	P_{Av}, cc.	μ Debye	P_{Calc} cc.
25	1.0000	0.5605	76.7	1.39	
	0.8247	0.5535	83.0	1.48	83.1
	0.6668	0.5372	88.2	1.56	87.2
	0.5621	0.5128	89.8	1.59	89.8
	0.4665	0.4890	91.5	1.61	92.1
	0.2601	0.4306	95.7	1.68	96.3
	0.0000	0.3392*b			
50	1.0000	0.5503	76.3	1.42	
	0.8247	0.5418	81.1	1.51	81.0
	0.6668	0.5230	85.2	1.58	84.9
	0.5621	0.5025	87.3	1.61	87.2
	0.4665	0.4795	88.7	1.64	89.4
	0.2601	0.4267	93.6	1.71	93.4
	0.0000	0.3392*b			

*a w_A is the weight fraction of *p*-chlorostyrene in the copolymer. p_2 is the specific polarization of the copolymer. P_{Av} is the average molecular polarization of a *p*-chlorostyrene monomer unit in the copolymer molecule. μ is the dipole moment calculated from the equation

$$\mu=0.0128\times[\{P_{Av}-(\mathrm{MR})_D\}T]^{1/2}$$

in which 38.2 cc. was used as the value of $(\mathrm{MR})_D$ for the *p*-chlorostyrene monomer unit.

*b The value of p_{St} for polystyrene.

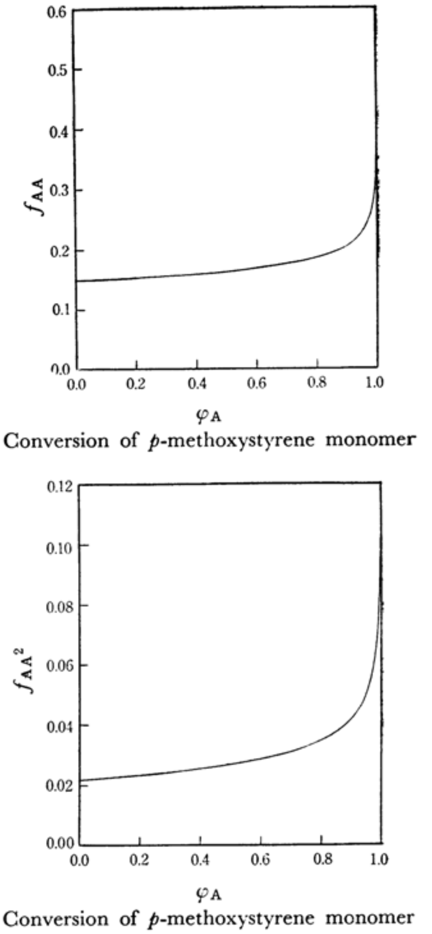

Fig. 4. Up, probability of AA sequence arising in copolymer; under, probability of double AA sequence arising in copolymer. $x_0=0.1749$

TABLE III. PROBABILITIES OF AN AA SEQUENCE AND A DOUBLE AA SEQUENCE ARISING IN THE COPOLYMERS

p-Methoxystyrene - styrene copolymers

x	$\overline{f_{AA}}$	$\overline{f_{AA^2}}$
1.0000	1.0000	1.0000
0.8347	0.8344	0.6997
0.5799	0.5780	0.3361
0.4075	0.4050	0.1659
0.1749	0.1730	0.0303
0.0000	0.0000	0.0000

p-Chlorostyrene - styrene copolymers

x	$\overline{f_{AA}}$	$\overline{f_{AA^2}}$
1.0000	1.0000	1.0000
0.7795	0.7911	0.6261
0.6007	0.6186	0.3826
0.4910	0.5113	0.2615
0.3966	0.4048	0.1749
0.2039	0.2175	0.0507
0.0000	0.0000	0.0000

x is the mole fraction of the polar monomer A in the copolymer.

may treat the experimental results of the *p*-chlorostyrene - styrene copolymers in the way described above. Figures 6—10 give the f_{AA} and f_{AA}^2 values for the copolymers of *p*-chlorostyrene and styrene as functions of the conversion of the *p*-chlorostyrene monomer. The monomer reactivity ratios for this copolymer system, $r_1=1.038$ and $r_2=0.786$, were employed[17]: the values of $\overline{f_{AA}}$ and $\overline{f_{AA}^2}$ calculated from these figures are shown in Table III.

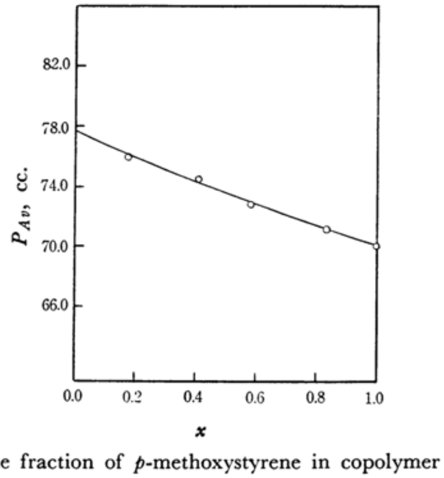

Fig. 5. Average dielectric polarization vs. composition.
——; theoretical curve from Eq. 5
○ ; experimental values (at 20°C)

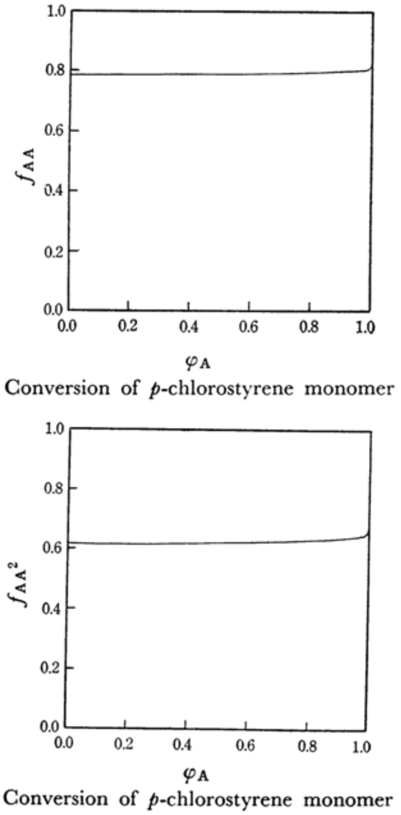

Fig. 6. Up, probability of AA sequence arising in copolymer; under, probability of double AA sequence arising in copolymer. $x_0=0.7795$

By substituting the values of $\overline{f_{AA}}$ and $\overline{f_{AA}^2}$ and the experimental data of P_{Av} into Eq. 5, the values of P_{Av} and P_{BB} were obtained by the method of least squares. The last columns in Table I and Table II give the theoretical values of the average

TABLE IV. VALUES OF MOLECULAR POLARIZATION AND DIPOLE MOMENT FOR THE THREE TYPES OF POLAR MONOMER UNIT ASSUMED IN Eq. 4

Temp. °C	P_{AA} cc.	P_{AB} cc.	P_{BB} cc.	μ_{AA} Debye	μ_{AB} Debye	μ_{BB} Debye
p-Methoxystyrene - styrene copolymers						
20	70.1	73.2	77.7	1.21	1.27	1.35
50	68.8	71.2	75.1	1.24	1.29	1.37
p-Chlorostyrene - styrene copolymers						
25	77.7	90.8	100.8	1.39	1.60	1.75
50	76.3	87.8	97.8	1.42	1.62	1.78

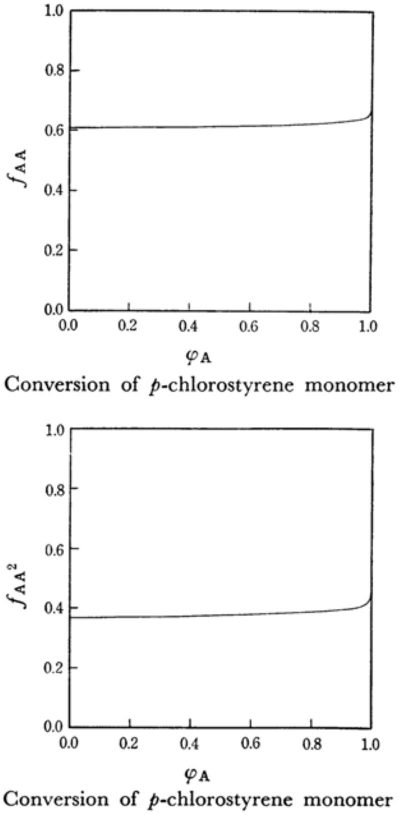

Fig. 7. Up, probability of AA sequence arising in copolymer; under, probability of double AA sequence arising in copolymer. $x_0=0.6007$

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[17] F. M. Lewis, C. Walling, W. Cummings, F. R. Briggs and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1519 (1948).

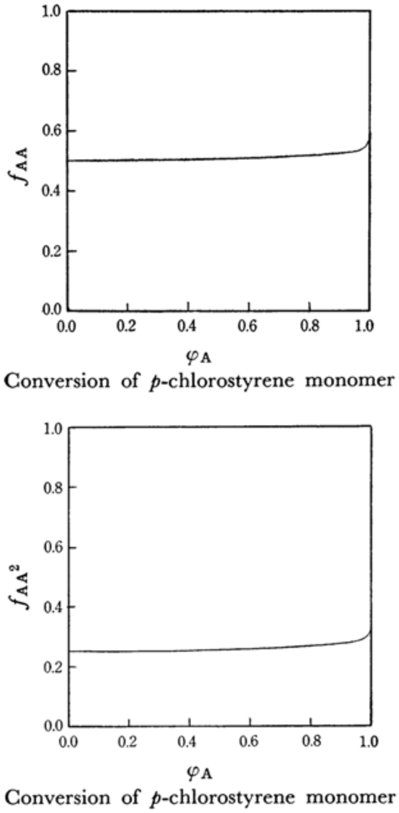

Fig. 8. Up, probability of AA sequence arising in copolymer; under, probability; of double AA sequence arising in copolymer. $x_0=0.4910$

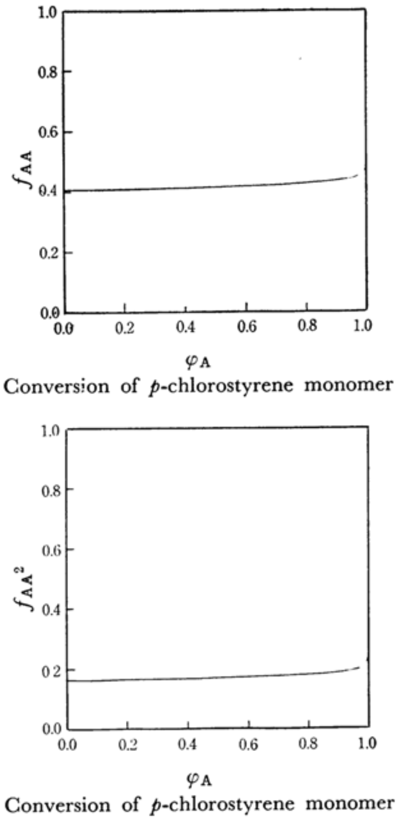

Fig. 9. Up, probability of AA sequence arising in copolymer; under, probability of double AA sequence arising in copolymer. $x_0=0.3966$

molecular polarization obtained by Eq. 5 for the polar monomer unit in the copolymers. These values are also shown in Fig. 5 and Fig. 11 as a function of the composition of copolymers and compared with the experimental values. The good agreement of these results with the experimental values over the whole range of composition implies that the values of P_{AA}, P_{AB} and P_{BB} are practically constant and that the assumptions made in the theory are reasonable in the case of the copolymers of both *p*-methoxystyrene - styrene and *p*-chlorostyrene - styrene. The values obtained for P_{AA}, P_{AB} and P_{BB} are given in Table IV. The values of μ_{AA}, μ_{AB} and μ_{BB} were calculated by using Eq. 3.

The difference in the values of μ at 20°C and 50°C may be interpreted in terms of the internal rotation in the polymer molecule. It is known that in a chain molecule of polymer, the internal rotation around the C–C bonds of the chain skeleton is not free and that three energetically-favored positions persist, i. e., one "trans" and two "gauche" configurations.[18] The temperature dependence of the potential energy for the restricted rotation may explain the difference in values of μ at 20°C and 50°C.

It was noticed that the shape of the curves in Figs. 5 and 11 is not similar to that for the methyl methacrylate - styrene copolymers or methyl acrylate - styrene copolymers; i. e., in Figs. 5 and 11, the curve of P_{Av} seems to be almost linear with respect to x. This may be because, in the case of *p*-methoxystyrene - styrene copolymers and *p*-chlorostyrene - styrene copolymers, the difference between the values of P_{AA} and P_{BB} is rather small, the value of P_{AB} is close to the average of P_{AA} and P_{BB}, and the value of f_{AA} is almost equal to that of the mole fraction, x, therefore, Eq. 5 can be regarded as approximately a linear function of x.

According to the definition of P_{BB}, μ_{BB} is the dipole moment of the polar group which is separated by nonpolar groups from the influence of the interactions of the other polar groups in the same copolymer molecule; its value may be compared with that of the dipole moment of the polar group in an isolated state, which can be obtained from measurements in a nonpolar solvent. The experimental value of the dipole moment of *p*-methoxyethyl-benzene is not knwon, but by taking the

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[18] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York (1953).

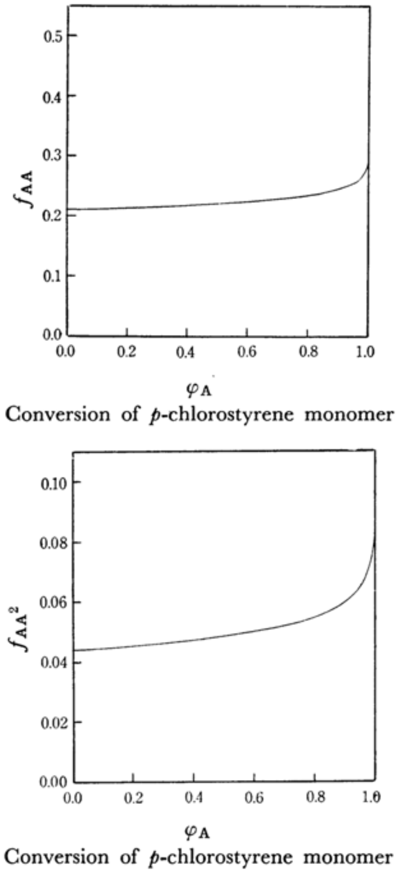

Fig. 10. Up, probability of AA sequence arising in copolymer; under, probability of double AA sequence arising in copolymer. $x_0=0.2039$

vector sum of the moment of anisole, 1.25 D,[19] and that of toluene, 0.37 D,[19] we can obtain 1.16 D as the calculated value. The value of μ_{BB} in the *p*-methoxystyrene - styrene copolymer was 1.35—1.37 D. The dipole moment of *p*-chlorotoluene is known to be 1.94 D,[19] which may be compared with the μ_{BB} values of 1.75—1.78 D in the *p*-chlorostyrene - styrene copolymer. In the above comparison, it can be seen that the values of μ_{BB} are always a little smaller than those of the moments of the polar groups in the isolated state. These differences may be due to the effect of the induced moments of the neighboring styrene monomer units, which are induced on benzene nuclei by the polar group under consideration. A comparison of the μ_{BB} value of the *p*-methoxystyrene unit with that of the *p*-chlorostyrene unit suggests that the inductive effect may be a little larger in the *p*-methoxystyrene - styrene copolymer than in the *p*-chlorostyrene - styrene copolymer, and that the average of the angle between the dipole moment of the polar group and the induced dipole moment may be nearer to 180° in the former than in the latter.

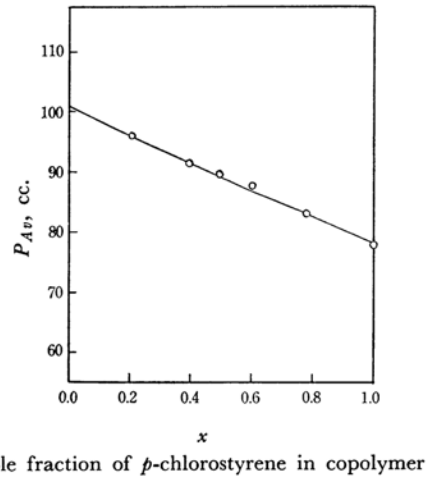

Fig. 11. Average dielectric polarization vs. composition.
——; theoretical curve from Eq. 5
○ ; experimental values (at 25°C)

It was noticed that the values of μ_{AB} are very near the average value of μ_{AA} and μ_{BB} in both copolymers. The value of $(\mu_{BB}-\mu_{AB})/(\mu_{AB}-\mu_{AA})$ is 0.08/0.06 at 20°C and 0.08/0.05 at 50°C in the *p*-methoxystyrene - styrene copolymer, and 0.15/0.21 at 25°C and 0.16/0.20 at 50°C in the *p*-chlorostyrene - styrene copolymer. The difference between μ_{BB} and μ_{AB} gives the decrease in the moment caused by the interaction effect of one neighboring polar group, which was introduced as a neighbor instead of the nonpolar styrene group, while the difference between μ_{AB} and μ_{AA} is the further decrease in the moment caused by the replacement of the neighboring styrene with a polar group. It appears that, in the *p*-methoxystyrene - styrene copolymer, the first decrease in the moment is a little larger than the second decrease, while the reverse is true in the *p*-chlorostyrene - styrene copolymer. However, the difference between $(\mu_{BB}-\mu_{AB})$ and $(\mu_{AB}-\mu_{AA})$ is so small in these copolymers that these two values may be considered to be almost equal to each other. In the copolymer in which there is a possibility of internal rotation within the polar group, the value of $(\mu_{BB}-\mu_{AB})$ should be much larger than that of $(\mu_{AB}-\mu_{AA})$, which was found in previous considerations of the methyl methacrylate - styrene copolymer and the methyl acrylate - styrene copolymer.

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[19] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Company, Inc., New York (1955).