

Dipole moments of copolymers in relation to the distribution of polar monomer unit sequences

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(Received 3 September 1990; revised 31 December 1990; accepted 21 January 1991)

A method for evaluating the dipole moments of copolymers in relation to the distribution of polar unit sequences is proposed. Experimental data on the synthesis and dipole moments of styrene-*p*-chlorostyrene and styrene-*p*-methoxystyrene copolymers were used to calculate the effective dipole moment of a polar unit in a copolymer. For this purpose, we assumed the following effective moment values for the corresponding polar unit sequences along the copolymer chains: when both of the nearest neighbours are polar, μ_{PP} , when one of the nearest neighbours is polar and the other is non-polar, μ_{PS} , and when both of the nearest neighbours are non-polar, μ_{SS} . The relative magnitudes of μ_{SS} , μ_{PS} and μ_{PP} calculated for both copolymers reflect the influence of dipole-dipole interactions on the effective dipole moment of a polar unit in a copolymer molecule.

(Keywords: dipole moment; poly(styrene-*co-p*-chlorostyrene); poly(styrene-*co-p*-methoxystyrene); sequence distribution; nearest neighbour interaction; microstructure)

INTRODUCTION

Physical properties of copolymers depend not only on their overall composition but also on the detailed arrangement of monomer units in the polymeric chain. For example, it has been known that for block and graft copolymers in which one type of monomer forms long sequences, several properties such as mechanical properties, micelle formation in solution and microphase separation are all different from those of the statistical or alternating copolymers that have the same composition¹.

Rotational isomeric state theory has been developed^{2,3} and during the past two decades it has been extensively used to calculate the dipole moments as well as other configuration-dependent properties of various polymers⁴⁻⁷ and copolymers⁸⁻¹¹.

Dipole moment measurements have proved to be a powerful tool in studying the conformation of polymers¹¹. In a polymer molecule the value of the dipole moment per polar unit, determined via dielectric constant measurements, is not the same as the dipole moment of the isolated unit. Rather it includes the effect of intramolecular interactions between the neighbouring polar units along the chain, i.e. the influence of the dipole-dipole interaction, steric hindrance, etc. Because of the effect of these interactions, the effective dipole moment of each polar unit in the polymer, μ , will be smaller than that of the isolated unit, μ_0 .

In a copolymer of a polar monomer with a non-polar monomer, the influence of dipole-dipole interactions may be reduced by the non-polar units which separate the polar units. An increase in the non-polar monomer content should decrease the dipole-dipole interactions along the chain and accordingly the value of μ will

approach μ_0 . This effect has been studied previously by investigating the dipole moments of polar styrene copolymers with different polar monomer content¹².

In this paper the relationship between the dipole moment and the microstructure of the copolymer, i.e. the distribution of polar and non-polar monomer units in the copolymer chain, was studied for poly(styrene-*co-p*-chlorostyrene) (S-PCS) and poly(styrene-*co-p*-methoxystyrene) (S-PMS) random copolymer systems.

THEORY

If only dipole-dipole interactions between nearest neighbours are considered, then the polar groups (P) in the copolymer molecule can be classified into three types with different effective dipole moments. This can be represented as:



where S represents the non-polar styrene monomer residue.

In type I, for which the effective dipole moment is represented by μ_{PP} , both neighbouring units are polar; in type II one neighbour is polar and the other is non-polar, and the effective dipole moment is μ_{PS} ; and type III is the case in which both neighbours are non-polar and the effective dipole moment is denoted by μ_{SS} . Therefore, the mean-square dipole moment of the polar group in the copolymer molecule $\overline{\mu^2}$, can be expressed as:

$$\overline{\mu^2} = \mu_{PP}^2 F_{PP} + \mu_{PS}^2 F_{PS} + \mu_{SS}^2 F_{SS} \quad (1)$$

where F_{PP} , F_{PS} and F_{SS} are the fractions of all the P units having nearest neighbours P and P, P and S, and S and S, respectively.

F_{PP} , F_{PS} and F_{SS} are given by the following equations, provided that f_{PP} is the probability of a PP sequence arising in the copolymer molecule:

$$F_{PP} = \overline{f_{PP}^2} \quad (2)$$

$$F_{PS} = 2 \overline{f_{PP}(1 - f_{PP})} = 2(\overline{f_{PP}} - \overline{f_{PP}^2}) \quad (3)$$

$$F_{SS} = \overline{(1 - f_{PP})^2} = 1 - 2\overline{f_{PP}} + \overline{f_{PP}^2} \quad (4)$$

where the bars denote average values and $\overline{f_{PP}^2}$ is the average probability of a double PP sequence (PPP triad) arising in the copolymer molecule. By using equations (2)–(4), equation (1) can be transformed:

$$\overline{\mu^2} = \overline{f_{PP}^2} \mu_{PP}^2 + 2(\overline{f_{PP}} - \overline{f_{PP}^2}) \mu_{PS}^2 + (1 - 2\overline{f_{PP}} + \overline{f_{PP}^2}) \times \mu_{SS}^2 \quad (5)$$

A similar relation has been proposed by Kotera *et al.*¹³ in terms of average molar polarizations of different types of polar groups in the copolymer molecule.

The probability of a growing chain radical which has a P unit at the end to add another P unit during the propagation of the chain, f_{PP} , is related to the mole fraction of polar monomer in the reaction mixture, X , and to its monomer reactivity ratio, r , by the following equation¹⁴:

$$f_{PP} = \frac{r_1 X}{r_1 X + 1 - X} \quad (6)$$

Denoting the conversion of polar monomer by φ_1 , the average values of f_{PP} and f_{PP}^2 can be written as:

$$\overline{f_{PP}} = \frac{\int_0^{\varphi_1} f_{PP} d\varphi}{\int_0^{\varphi_1} d\varphi} \quad \text{and} \quad \overline{f_{PP}^2} = \frac{\int_0^{\varphi_1} f_{PP}^2 d\varphi}{\int_0^{\varphi_1} d\varphi} \quad (7)$$

On the other hand, one can obtain the following expression by integration of the copolymer composition equation¹⁵:

$$(1 - \varphi) = \left(\frac{X}{X_0}\right)^{1/(1-r_2)} \left(\frac{1-X}{1-X_0}\right)^{r_1/(1-r_1)} \left[\frac{(r_1+r_2-2)X - (r_2-1)}{(r_1+r_2-2)X_0 - (r_2-1)}\right]^{(r_1 r_2 - 1)/[(1-r_1)(1-r_2)]} \quad (8)$$

where X_0 is the mole fraction of the polar monomer in the initial monomer mixture and r_1 and r_2 are the reactivity ratios of polar and non-polar monomers, respectively.

EXPERIMENTAL

Copolymer preparation

The S-PCS and S-PMS statistical copolymers were synthesized by free radical copolymerization. Monomers were freshly distilled under reduced pressure just before use. They were mixed in proper molar ratios so that the whole composition range could be covered. Benzoyl peroxide (0.1 mol%) was added as an initiator into each copolymerization mixture. They were evacuated and sealed. Polymerizations were carried out in a constant temperature bath at 60°C. Per cent conversions were kept

low. The copolymers were dissolved in toluene, precipitated with methanol, and dried in a vacuum oven.

Dipole moment measurements

Capacitance measurements were carried out at low frequencies (1–10 kHz) using a General Radio Company type 1620 A capacitance measuring assembly. Toluene was used as the solvent in all of the dielectric constant measurements.

The details of the synthesis of the copolymer samples and the dipole moment determinations have been reported previously^{12,14}.

RESULTS AND DISCUSSION

The data for the polymerization of S-PCS and S-PMS copolymers are given in *Tables 1* and *2*, respectively. Per cent conversions were kept low during copolymerization. Compositions were calculated from the copolymer composition equation¹⁵. The values of the reactivity ratios used were r_1 (styrene) = 0.74, r_2 (*p*-chlorostyrene) = 1.24 for S-PCS polymerization¹⁶; and r_1 (styrene) = 1.05, r_2 (*p*-methoxystyrene) = 0.79 for S-PMS copolymerization at 60°C¹⁵.

The mean-square dipole moment per polar unit in the copolymer chain, $\overline{\mu^2}$, was determined by the Guggenheim–Smith method^{17,18} from dielectric constant and refractive index increment measurements of the samples in dilute toluene solutions¹⁴. Experimental $\overline{\mu^2}$ values are included in *Tables 1* and *2*.

Since f_{PP} in equation (6) (the probability of a polar unit in the chain to add another polar monomer rather than a non-polar styrene monomer) is not expressed as an explicit function of φ (conversion of polar monomer), the integrations in equation (7) cannot be performed analytically. Therefore, the numerical relationship between f_{PP} and X (the mole fraction of polar monomer in the monomer mixture) and X and φ were obtained using a computer. The X values were varied from 0 to X_0 by small increments (0.0025), and the corresponding f_{PP} and φ values were calculated from equations (6) and

Table 1 Data for the polymerization and dipole moments of S-PCS

Sample no.	X_0^a	F_2^b	$\overline{\mu^2}^c$ (D ²)
S-PCS-1	0.205	0.247	2.67
S-PCS-2	0.789	0.802	1.76
PPCS	1.000	1.000	1.65

^a Mole fraction of polar monomer in the monomer feed¹²

^b Mole fraction of polar monomer in the copolymer¹²

^c Mean-square dipole moment per polar unit at 25°C in toluene solution¹²

ID = 3.34×10^{-30} C m

Table 2 Data for the polymerization and dipole moments of S-PMS

Sample no.	X_0^a	F_2^b	$\overline{\mu^2}^c$ (D ²)
S-PMS-1	0.168	0.157	1.56
S-PMS-2	0.352	0.328	1.23
S-PMS-3	0.514	0.480	1.08
S-PMS-4	0.757	0.721	1.01
PPMS	1.000	1.000	0.78

Footnotes as in *Table 1*

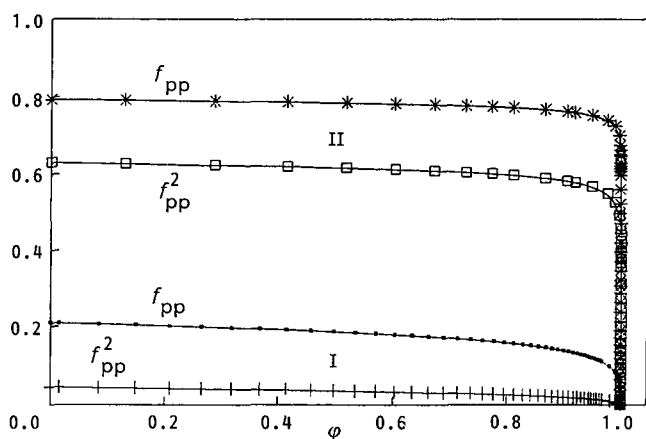


Figure 1 Probability of PP sequence (f_{pp}) and a double PP sequence (f_{pp}^2) for S-PCS copolymers: (I) for S-PCS-1 ($\varphi_1 = 0.18$); (II) for S-PCS-2 ($\varphi_1 = 0.21$)

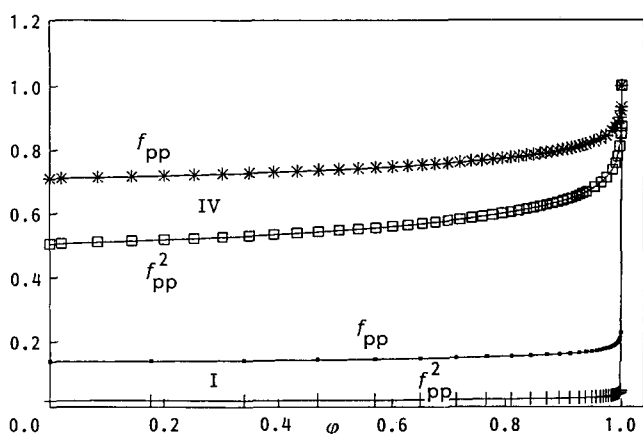


Figure 2 Probability of PP sequence (f_{pp}) and a double PP sequence (f_{pp}^2) for S-PMS copolymers: (I) for S-PMS-1 ($\varphi_1 = 0.21$); (IV) for S-PMS-4 ($\varphi_1 = 0.10$)

(8), respectively. Then, f_{pp} and f_{pp}^2 values were plotted against corresponding φ values. These plots are given in *Figure 1* for S-PCS copolymers and in *Figures 2 and 3* for S-PMS copolymers. The average value of f_{pp} and f_{pp}^2 for each sample was calculated by finding the area under the curve from $\varphi = 0$ to $\varphi = \varphi_1$ (φ_1 denoting the fractional conversion of polar monomer at the end of copolymerization). The $\overline{f_{pp}}$ and $\overline{f_{pp}^2}$ values thus determined are listed in *Table 3*.

Consequently, the values of μ_{PS}^2 and μ_{SS}^2 were calculated from equation (5) for S-PCS and S-PMS copolymers by using experimental μ^2 values. For this calculation, μ^2 values of homopolymers PPCS and PPMS were used instead of μ_{PP}^2 in equation (5). In the case of S-PMS copolymers, since there were more than two copolymer samples, i.e. more than two equations to solve μ_{PS}^2 and μ_{SS}^2 , the method of least squares was used to obtain the best value to fit the experimental data.

The values of μ_{PS} and μ_{SS} for S-PCS or S-PMS copolymers calculated by this method are given in *Table 4*. In both cases μ_{PS} has a larger value compared with μ_{PP} and the value of μ_{SS} is close to the dipole moment of the isolated unit μ_0 ($\mu_0 = 2.00$ D for *p*-chloroethylbenzene in benzene and $\mu_0 = 1.21$ D for *p*-methoxytoluene in benzene)¹⁹. A small difference between μ_{SS} and μ_0 might be due to the contribution of the next to nearest

neighbour interactions, and the restriction of internal rotation due to steric hindrance.

When a polar unit in a copolymer chain has one of its nearest neighbours as polar, these units prefer to be oriented in opposite directions, therefore the contribution of the polarity to the dielectric constant will decrease. This causes the experimental dipole moment to be less than the dipole moment of the isolated polar unit $\mu_{PS} < \mu_{SS}$. Furthermore, when both of the nearest neighbours are polar, attenuation of the effective dipole moment will be even more pronounced; μ_{PP} has the smallest value accordingly.

The effect of steric hindrance on the restriction of internal rotation and the attenuation of the effective dipole moment must be less compared with dipole-dipole interactions because the non-polar monomer chosen in this study, styrene, is similar in structure to the polar monomers PCS and PMS. Most of the steric

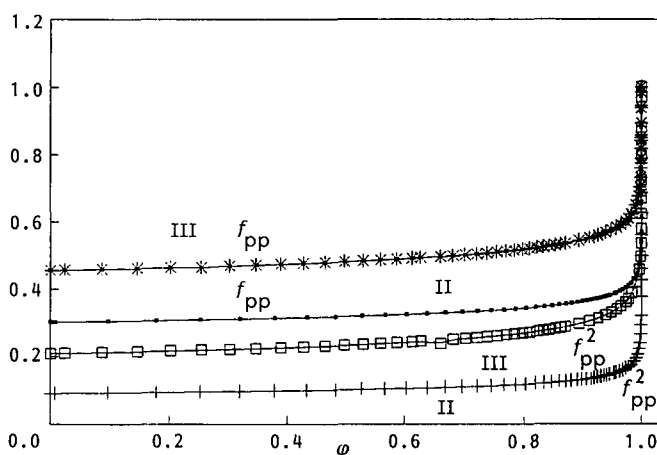


Figure 3 Probability of PP sequence (f_{pp}) and a double PP sequence (f_{pp}^2) for S-PMS copolymers: (II) for S-PMS-2 ($\varphi_1 = 0.11$); (III) for S-PMS-3 ($\varphi_1 = 0.12$)

Table 3 Average probabilities of a PP sequence and PPP sequence arising in the copolymer

Sample no.	$\overline{f_{pp}}$	$\overline{f_{pp}^2}$
S-PCS copolymers		
S-PCS-1	0.207	0.044
S-PCS-2	0.787	0.626
PPCS	1.000	1.000
S-PMS copolymers		
S-PMS-1	0.140	0.020
S-PMS-2	0.303	0.089
S-PMS-3	0.458	0.209
S-PMS-4	0.713	0.507
PPMS	1.000	1.000

Table 4 Values of dipole moments for the three types of polar units assumed in equation (1)

	μ_{PP} (D)	μ_{PS} (D)	μ_{SS} (D)	μ_0 (D)
S-PCS copolymers				
This work at 25°C	1.39	1.60	1.75	2.00
Reference 13 at 25°C	1.29	1.39	1.79	1.94
S-PMS copolymers				
This work at 25°C	0.88	0.96	1.30	1.21
Reference 13 at 20°C	1.21	1.27	1.35	1.16

hindrance arises due to the bulky benzene ring which is the same in both polar and non-polar nearest neighbours. Therefore, the difference in the values of μ_{SS} , μ_{PS} and μ_{PP} only reflects the influence of dipole-dipole nearest neighbour interactions.

In Table 4 results of this work are compared with the μ_{PP} , μ_{PS} and μ_{SS} values found by Kotera *et al.*¹³ for the same copolymer systems by assuming that molar polarizations of the three types of polar units are related to the average molar polarization of the polar unit by an equation similar to equation (1). There is good agreement between our results and the results of Kotera *et al.*¹³ which may confirm that equation (1) is valid for polar-non-polar copolymer systems.

ACKNOWLEDGEMENT

ZK would like to thank the Middle East Technical University for financial support of the research project AFP 90-01-03-07.

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