References and Notes

(1) Hong, S. H.; McHugh, V. M. Review of polymerization and properties of aminoalkyl acrylates and aminoalkyl methylacrylates, with 31 references. NTIS No. ADA 197705, July 1988.
(2) Hong, S. H.; McHugh, V. M. Review of preparation and properties of polymers from copolymerization of aprotic acrylic monomers with protic acrylic monomers, with 57 references. NTIS No. ADA 197467, July 1988.
(3) Debye, P. *J. Phys. Colloid Chem.* **1947**, *51*, 18.
(4) Stockmayer, W. H.; Moore, L. D., Jr.; Fixman, M.; Epstein, B. N. *J. Polym. Sci.* **1955**, *16*, 517.
(5) Bushuk, W.; Benoit, H. *Can. J. Chem.* **1958**, *36*, 1616.
(6) Chu, B.; Ying, Q.; Lee, D.; Wu, D. *Macromolecules* **1985**, *18*, 1962. See references therein.
(7) Galin, J. C. *Report on Copolymers CM, K-125E and K-125G*; ICS: Strasbourg, France (private communication).
(8) Potts, M. K.; Hagnauer, G. L.; Dunn, D. A., private communication.
(9) Chu, B.; Wu, D. *Macromolecules* **1987**, *20*, 1606.

Registry No. Poly(iBMA-tBAEMA), 40008-96-6.

Miscibility of Poly(ethylene oxide) and Poly(styrene-*co*-acrylic acid) Blends

Won Ho Jo* and Sang Cheol Lee

Department of Textile Engineering, Seoul National University, Seoul 151-742, Korea.

Received July 5, 1989; Revised Manuscript Received October 25, 1989

ABSTRACT: The miscibility for blends of poly(ethylene oxide) (PEO) with poly(styrene-*co*-acrylic acid) (SAA) was examined as a function of the comonomer content of the copolymer. PEO was found to be miscible with SAA copolymers having an acrylic acid content higher than 7 mol %. The segmental interaction parameters were determined by combining the equilibrium melting point depression and a binary interaction model. These values suggest that both the specific interaction between ethylene oxide and acrylic acid segments and the intramolecular repulsive force in SAA copolymer are responsible for the miscibility. The minimum acrylic acid content in SAA for the blend to be homogeneous was predicted to be 7.7 mol % from the binary interaction model and the calculated values of segmental interaction parameters.

Introduction

In recent years, the origins of miscibility between polymer pairs have been understood based on theoretical backgrounds and experimental results.[1,2] Thermodynamically, polymer–polymer miscibility requires a negative heat of mixing. Therefore, miscible blends will be formed if there are some specific intermolecular interactions between polymer pairs such as hydrogen bonding, etc.[3]

On the other hand, many random copolymers have been reported to be miscible with homopolymers in spite of the absence of specific interactions.[4–8] In order to interpret this phenomenon, Kambour et al.[9] proposed a binary interaction model for mixtures of a homopolymer and a random copolymer based on the Flory–Huggins lattice model. According to this model, the mutual repulsive force between dissimilar segments in the copolymer can lead to the negative heat of mixing necessary to attain miscibility. More recently, Paul et al.,[10–14] Karasz et al.,[15,16] and others[17–19] have further extended the above binary interaction model to several types of blends containing copolymers and applied the model to interpret the effect of the copolymer composition on the miscibility of blends.

According to the binary interaction model, miscible blend systems can be developed by designing copolymers through appropriate choices of comonomers and copolymer compositions. Besides the mutual repulsive force between dissimilar segments in the copolymer, some specific interactions between polymer pairs also play an important role for inducing miscibility. Considering the above two factors, in this study the acrylic acid (AA) was incorporated onto polystyrene (PS) to enhance the miscibility of poly(ethylene oxide) (PEO) and polystyrene. The primary objectives of this study are (1) to investigate the effect of copolymer composition on the miscibility, (2) to determine the segmental interaction parameters by combining the binary interaction model and the data obtained by analysis of the equilibrium melting point depression, (3) to ascertain which interactions are responsible for the miscibility, (4) to predict the critical copolymer composition for the mixture to be miscible, and (5) to clarify the nature of the specific intermolecular interactions by using spectroscopic analysis.

Experimental Section

Materials. Poly(ethylene oxide) ($M_w = 1.0 \times 10^5$, $T_g = -56$ °C) was obtained from Aldrich Co. It was used as received without further purification. The poly(styrene-*co*-acrylic acid) (SAA) was synthesized in a sealed glass ampule by bulk polymerization at 60 °C, using benzoyl peroxide as an initiator. The copolymer formed was isolated by pouring the reaction mixture into *n*-hexane and dried in a vacuum oven at 100 °C for 2 days. The maximum degree of conversion was controlled to about 7 wt %. The acrylic acid content of the copolymer was determined by titration in benzene/methanol (9/1, v/v) with a standardized methanolic NaOH solution using phenolphthalein as an indicator. The intrinsic viscosity was measured at 25 °C in dilute tetrahydrofuran solution by extrapolation to zero concentration. The copolymer composition and other properties are listed in Table I.

Preparation of Blends. The blends were prepared by dissolving the component polymers in benzene/methanol (9/1, v/v). The solutions were cast on an aluminum dish, and most of solvent was allowed to evaporate slowly in the air at room temperature. The resulting films were then completely dried in a vacuum oven at 60 °C for at least 3 days.

0024-9297/90/2223-2261$02.50/0

Table I
Properties of SAA Copolymers

sample	copolymer composition, mol % of AA	intrinsic viscosity, dL/g	T_g, °C
SAA7	7.0	1.24	108
SAA15	15.0	1.19	115
SAA19	19.0	1.08	119
SAA29	29.0	0.93	125

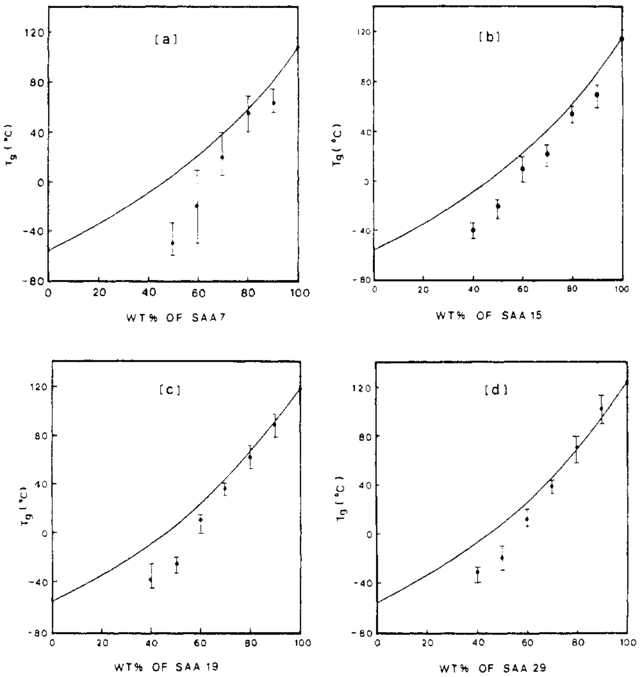

Figure 1. Glass transition behaviors for (a) PEO/SAA7, (b) PEO/SAA15, (c) PEO/SAA19, and (d) PEO/SAA29 blends.

Thermal Analysis. Thermal analysis was performed on a Du Pont 910 differential scanning calorimeter (DSC) equipped with a mechanical cooling accessory. Samples were first maintained at 130 °C for 5 min to destroy the solution history. They were then cooled to -60 °C at a rate of 10 °C/min and heated to 150 °C at a rate of 20 °C/min. Using this dynamic program, we determined thermal properties such as melt crystallization temperature (T_{cm}), melting temperature (T_m), heat of fusion (ΔH_f), and glass transition temperature (T_g). The isothermal crystallization from the melt was also examined by DSC. The samples were melted at 85 °C for 5 min, cooled quickly to the crystallization temperature (T_c), and then kept at T_c for at least 20 min. After isothermal crystallization was completely terminated, the samples were then cooled to 20 °C and heated to 100 °C with a heating rate of 20 °C/min for measuring the melting temperature (T_m).

FTIR Spectroscopy. FTIR spectroscopy was used to examine the interaction in the blends. Infrared spectroscopy was used to examine the interaction in the blends. Infrared spectra were obtained by using a Digilab FTS-20/80 spectrometer. Sixty-four scans at a resolution of 2 cm^{-1} were signal averaged and stored on a magnetic disk system.

Results and Discussion

Thermal Properties and Miscibility. The glass transition behaviors are shown in Figure 1. The glass transition temperature was taken as the midpoint of the heat capacity change, and the glass transition range was taken as the temperature range between the two onset points of the low-temperature and high-temperature base lines. The glass transition temperatures of the blends with higher PEO contents were not observed since PEO in the blends crystallized sufficiently on cooling. Blends of PEO/SAA15, PEO/SAA19, and PEO/SAA29 have a single glass transition between those of components. The samples rich in SAA were transparent at room temperature. However, the blend samples became increasingly less transparent with increasing the PEO contents owing to the crystallization of PEO. All of the blend samples were transparent just above the melting point of PEO. These mixtures are clearly miscible according to the glass transition behavior and transparency. The mixture of PEO and SAA7 shows a single but very broad glass transition. The samples with low PEO contents (up to 30 wt %) were transparent, but at higher PEO contents the samples were cloudy even above the melting temperature of PEO, indicating that the PEO/SAA7 blend is not completely miscible over the entire blend ratio. The composition dependence of the glass transition temperature is compared with the Fox equation.[20] The glass transition temperature deviates more negatively from the Fox equation as the AA content in SAA decreases. This result agrees well with the fact that the number of the intermolecular interaction between PEO and SAA copolymer chain decreases with increasing the AA content of SAA. Consequently, the more the AA content in SAA, the better the miscibility.

Table II
Thermal Properties of PEO/SAA Blends

sample	blend ratio (wt/wt)	T_{cm}, °C	T_m, °C	$\Delta H_f°$, J/g[a]
PEO/SAA7	40/60		51.3	16.0
	50/50	9.0	52.2	83.4
	60/40	24.9	56.9	103.0
	70/30	35.7	58.8	123.6
	80/20	37.9	59.9	127.5
	90/10	38.5	60.0	132.2
PEO/SAA15	50/50		51.5	55.8
	60/40		51.6	72.5
	70/30	18.6	57.0	125.7
	80/20	30.1	58.3	137.5
	90/10	36.8	58.9	133.0
PEO/SAA19	50/50		53.5	48.8
	60/40	5.2	53.5	66.7
	70/30	17.1	55.7	122.6
	80/20	30.3	56.7	136.3
	90/10	37.0	59.8	127.8
PEO/SAA29	50/50		49.9	9.4
	60/40	-5.1	51.3	50.2
	70/30	5.0	52.1	78.6
	80/20	26.9	55.2	81.9
	90/10	31.9	61.7	84.4

[a] The heat of fusion for the pure PEO fraction.

Table II indicates that at higher PEO contents, PEO crystallizes from the molten mixture of PEO and SAA on cooling. The peak temperature of the melt crystallization decreases with increasing the SAA content in the blend. The peak temperature also decreases with increasing the AA content in the SAA copolymer at the same blend ratio. When the sample was reheated after cooling, the cold crystallization also occurred at concentrations of higher than 50 wt % PEO for PEO/SAA7, whereas the crystallization occurred at a concentration higher than 60 wt % PEO for PEO/SAA15, PEO/SAA19, and PEO/SAA29. This phenomenon suggests that the SAA in the blend hinders the crystallization of PEO, which is a typical phenomenon of a miscible blend in which the glass transition of an amorphous polymer is higher than that of a crystalline component. This result can be also supported by the data of heat of fusion. If the SAA copolymer has no effect on the crystallization of PEO, the heat of fusion for the pure PEO fraction must be constant for all the blends. However, the heat of fusion for the pure PEO fraction decreases with increasing the SAA concentration in the blend and with increasing the SAA content in SAA at the given blend ratio.

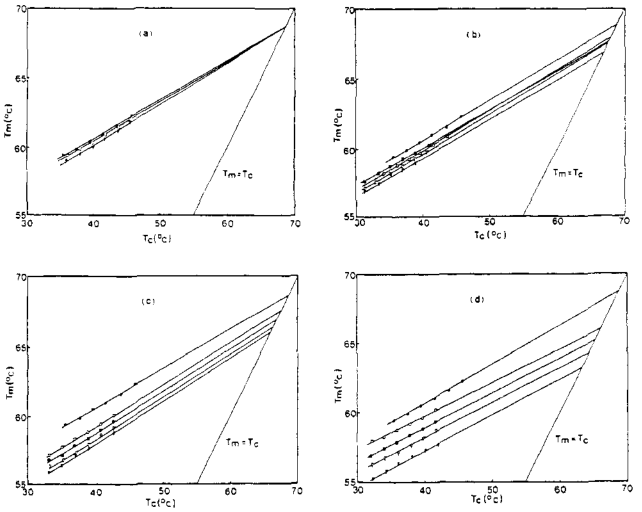

Figure 2. Hoffman–Weeks plots for (a) PEO/SAA7, (b) PEO/SAA15, (c) PEO/SAA19, and (d) PEO/SAA29 blends: (●) 100, (□) 85, (■) 80, (▽) 75, and (▼) 70 wt % PEO.

Analysis of Melting Point Depression. The melting point of a miscible polymer blend is depressed due to both the morphological effect and the thermodynamic reason. To eliminate the morphological effect from the melting point depression, the method of Hoffman and Weeks[21] has been used, and the equilibrium melting temperatures for pure PEO ($T_m{}^\circ$) and blends ($T_{mb}{}^\circ$) of given compositions were determined. Figure 2 represents the Hoffman–Weeks plots to obtain the equilibrium melting points for pure PEO and PEO/SAA blends. The $T_{mb}{}^\circ$ values for PEO/SAA7 blends are almost the same as the $T_m{}^\circ$. However, $T_{mb}{}^\circ$ values for the other blends decrease with increasing the content of SAA. This trend is more prominent for the blend of higher AA content in SAA. Generally, the blend which is immiscible or partially miscible does not show the depression of equilibrium melting point. But in the case of a miscible blend, especially containing the specific interactions between the components, the $T_{mb}{}^\circ$ is much more depressed with increasing the content of an amorphous polymer. Therefore, it is considered that the PEO/SAA7 blend is immiscible or partially miscible and that the other blends are miscible. These results are well consistent with the glass transition behavior.

In order to obtain quantitative information about the thermodynamic interactions in the blends, we used the Nishi–Wang equation:[22]

$$T_m{}^\circ - T_{mb}{}^\circ = -T_m{}^\circ \frac{BV_{2u}}{\Delta H_{2u}} \phi_1{}^2 \tag{1}$$

where $\Delta H_{2u}/V_{2u}$ means the latent heat of fusion of 100% crystalline component per unit volume, B is the interaction parameter between blend components, and ϕ_1 is the volume fraction of the amorphous component. As shown in Figure 3, the melting point depressions, ΔT_m, for PEO/SAA15, PEO/SAA19, and PEO/SAA29 increase linearly with $\phi_1{}^2$. The weight fractions were converted into volume fractions by using the molar volumes of monomeric units determined by group contribution method.[23] By use of eq 1 and the data of $B_{2u} = 41.4$ and $\Delta H_{2u} = 1980$ cal/cm^2, B values were calculated from the slopes of Figure 3. The calculated values are as follows:

$B = -2.2 \pm 0.4$ cal/cm^3 for PEO/SAA15
$B = -3.3 \pm 0.6$ cal/cm^3 for PEO/SAA19
$B = -6.2 \pm 0.2$ cal/cm^3 for PEO/SAA29

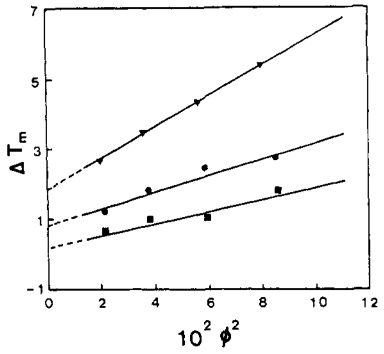

Figure 3. Plots of the equilibrium melting point depression vs the square of the volume fraction of SAA: (■) SAA15, (●) SAA19, and (▼) SAA29.

The negative B values for the above three systems support the fact that these systems are miscible in the melt, which is consistent with the results of the glass transition behavior. According to eq 1, the intercept of a plot of ΔT_m vs $\phi_1{}^2$ should be close to zero. However, the lines have finite values of the intercept. This phenomenon has been reported in other systems and may be due to the nonnegligible entropic effects which occur during mixing the two polymers.[24,25]

Application of Binary Interaction Model. The enthalpy of mixing is usually responsible for the miscibility, since the entropy change for the polymer mixture is negligibly small. The heat of mixing ΔH_m can be generally described by a Van Laar type expression:

$$\frac{\Delta H_m}{V} = B\phi_1\phi_2 \tag{2}$$

where V is the total volume of the mixture and ϕ_i is the volume fraction of the i component. For a binary mixture of a homopolymer A and a random copolymer C_yD_{1-y}, the B value of eq 2 can be expressed as

$$B = yB_{AC} + (1-y)B_{AD} - y(1-y)B_{CD} \tag{3}$$

Equation 3 shows that the overall interaction parameter B consists of the segmental interaction parameters between the segment pairs and does not depend on the blend ratio of two polymers. The interaction parameter should be negative for a polymer blend to be miscible, since the combinatorial entropy of mixing is close to zero. Thus, the miscibility of a blend containing copolymers depends on the segmental B_{ij} values and the copolymer compositions.

To apply the above binary interaction model to the PEO/SAA blend system, the monomeric units (or segments) are designated as A, C, and D for ethylene oxide, acrylic acid, and styrene, respectively. The copolymer compositions were converted in mole fractions into volume fractions by using the group contribution method. Now we can use eq 3 to calculate the segmental B_{ij} values. In the previous section, three overall B values were obtained for the blends containing the SAA copolymers of three different copolymer compositions. Thus, segmental interaction B_{ij} values can be calculated by fitting three B values into eq 3. The obtained values are

$$B_{AC} = -15.5 \text{ cal/cm}^3$$

$$B_{AD} = 1.8 \text{ cal/cm}^3$$

$$B_{CD} = 36.6 \text{ cal/cm}^3$$

Uncertainties of these values are estimated to be ±30% from error analysis. The negative value of B_{AC} indicates that the heat of mixing of poly(acrylic acid) (PAA) and

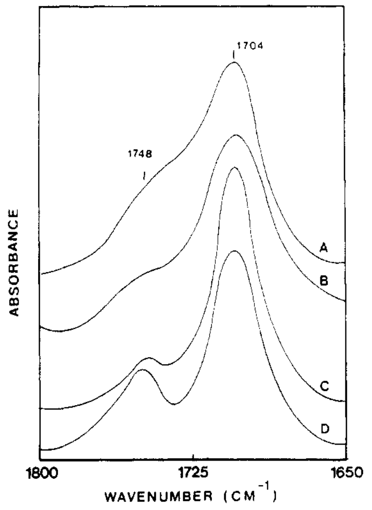

Figure 4. FTIR spectra for SAA copolymers in the range 1800–1650 cm^{-1}: (A) SAA29, (B) SAA19, (C) SAA15, and (D) SAA7.

PEO is exothermic. This result can be explained by the fact that PAA is miscible with PEO,[26] and the polymer pair forms a complex in aqueous systems by hydrogen bonding between the ether oxygens in PEO and the carboxylic acids in PAA.[27] The positive values of B_{AD} and B_{CD} suggest that the PEO/PS and PAA/PS blends are immiscible. The fact that the value of B_{CD} is relatively higher than the value of B_{AD} may be due to the presence of a strong self-association of carboxylic acid groups. The values also suggest that both the attraction (negative B_{AC}) between ethylene oxide and acrylic acid and the intramolecular repulsion (positive B_{CD}) in the SAA copolymer are primarily responsible for the miscibility. It is noteworthy that all the calculations are based on random mixing.

The binary interaction model predicts the minimum acrylic acid content in the SAA copolymer where the heat of mixing of the blend is zero. Equation 3 can be solved for y after setting the overall B value to zero and substituting the calculated segmental B_{ij} values. The calculated y value is approximately 7.7 mol %. Recalling the PEO/SAA7 blend is partially miscible, the model satisfactorily predicts the copolymer composition of SAA at which the blend system is marginally miscible.

Evidence of Specific Interaction in Spectroscopic Analysis. Figure 4 shows FTIR spectra of SAA copolymers in the range 1800–1650 cm^{-1} at room temperature. The SAA copolymers have absorption bands at 1704 cm^{-1} due to a normal mode involving C=O stretching for carboxylic acid groups dimerized by hydrogen bonding and at 1748 cm^{-1} due to C=O stretching for carboxylic acid groups where the carbonyl group is not hydrogen bonded. The relative magnitude of absorption at 1748 cm^{-1} increases with decreasing AA content in the SAA copolymer. Several workers[28-30] have studied infrared spectra for copolymers containing carboxylic acid groups. Lee et al.[29] reported that the majority of carboxylic acid groups of poly(ethylene-*co*-methacrylic acid) (EMAA) copolymers exist as intermolecular dimers with a characteristic infrared band at 1700 cm^{-1}, and there is little evidence of any significant absorption from the band attributed to the free carbonyl groups which have a characteristic frequency at about 1750 cm^{-1}. But in the SAA copolymers, the band at 1748 cm^{-1} due to the free carbonyl groups has a significant absorbance. Two possible factors can be considered: one is a steric effect given by a large phenyl side group in SAA which may shield the carboxylic group and the other is the difference in the chain flexibility. The EMAA copolymers is more flexible than the SAA copolymer.

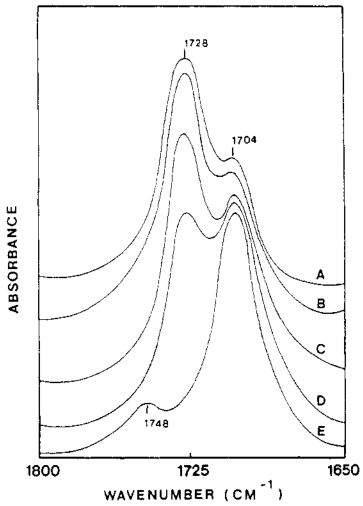

Figure 5. FTIR spectra for PEO/SAA15 blends in the range 1800–1650 cm^{-1}: (A) 80, (B) 60, (C) 40, (D) 20, and (E) 0 wt % PEO.

When the SAA15 is mixed with PEO, a new absorption band at 1728 cm^{-1} is observed as shown in Figure 5. The other blends show similar spectra (not shown here). As the PEO content in the blend increases, the band at 1728 cm^{-1} becomes dominant over the acid dimer band at 1704 cm^{-1}. Therefore, the band at 1728 cm^{-1} must be due to the carboxylic acid groups which form the intermolecular hydrogen bonds with the ether oxygens in PEO. If PEO and SAA are not mixed in molecular level, the absorption band at 1728 cm^{-1} must be very small or not detectable. Hence, the spectral change in the carbonyl region as a function of blend composition suggests that these blends are mixed in the molecular level.

References and Notes

(1) Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, 1978.
(2) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic Press: New York, 1979.
(3) Kleintjens, L. A., Lemstra, P. J., Eds. *Integration of Fundamental Polymer Science and Technology*; Elsevier Applied Science Publishers: London, 1986; p 119.
(4) Chiou, J. S.; Paul, D. R.; Barlow, J. W. *Polymer* **1982**, *23*, 1543.
(5) Shur, Y. J.; Randy, B. *J. Appl. Polym. Sci.* **1976**, *20*, 3121.
(6) Bywater, S. *Polym. Eng. Sci.* **1984**, *24*, 104.
(7) Hammer, C. F. *Macromolecules* **1971**, *4*, 69.
(8) Zabrzewski, G. A. *Polymer* **1973**, *14*, 347.
(9) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(10) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(11) Woo, E. M.; Barlow, J. W.; Paul, D. R. *Polymer* **1985**, *26*, 763.
(12) Fernandes, A. C.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci.* **1986**, *32*, 5357.
(13) Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1177.
(14) Min, K. E.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 2257.
(15) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(16) Shiomi, T.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1986**, *19*, 2274
(17) Suess, M.; Kressler, J.; Kammer, H. W. *Polymer* **1987**, *28*, 957.
(18) Kressler, J.; Kammer, H. W.; Schmidt-Noake, G.; Herzog, K. *Polymer* **1988**, *29*, 686.
(19) Chien, Y. Y.; Pearce, E. M.; Kwei, T. K. *Macromolecules* **1988**, *21*, 1616.
(20) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
(21) Hoffman, J. D.; Weeks, J. J. *J. Chem. Phys.* **1965**, *42*, 4301.
(22) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
(23) Van Krevelen, D. W. *Properties of Polymers*; Elsevier Scientific: Amsterdam, 1976; Chapter 4.

Macromolecules **1990,** *23,* 2265–2269

(24) Martuscelli, E.; Pracella, M.; Yue, W. P. *Polymer* **1984,** *25,* 1097.
(25) Min, K. E.; Chiou, J. S.; Barlow, J. W.; Paul, D. R. *Polymer* **1987,** *28,* 1721.
(26) Smith, K. L.; Smith, A. E.; Winslow, A. E.; Peterson, D. E. *Ind. Eng. Chem.* **1959,** *51,* 1361.
(27) Bailey, F. E.; Lundberg, R. D.; Callard, R. W. *J. Polym. Sci.* **1964,** *A2,* 845.
(28) Coleman, M. M.; Skrovanek, D. J.; Hu, J.; Paiter, P. C. *Macromolecules* **1988,** *21,* 59.
(29) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988,** *21,* 346.
(30) Lichkus, A. M.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988,** *21,* 2636.

Registry No. SAA (copolymer), 25085-34-1; PEO, 25322-68-3.

Molecular Fluctuations in the Packing of Polymeric Liquid Crystals

Rudi Podgornik[†] and V. Adrian Parsegian[*]

Section on Molecular Forces and Assembly, NIDDK, and Physical Sciences Laboratory, DCRT, National Institutes of Health, Bethesda, Maryland 20892. *Received July 10, 1989; Revised Manuscript Received September 5, 1989*

ABSTRACT: Recent measurements of forces between DNA polyelectrolytes have shown a direct and continuous coupling between intermolecular forces and molecular disorder in lattices of interacting particles. Over a wide range of conditions the work of assembly is dominated by the configurational entropy of molecules restricted by repulsive forces from their neighbors. This observed entropic force decays half as fast as what is predicted from the decay lengths for an electrostatic double layer or hydration forces between parallel molecules. It cannot be fit by the traditional model of flexible molecules with an effective hard wall radius. In this paper we develop a statistical mechanical model of a Gaussian randomly walking polymer surrounded by an effective "tube" of its neighbors, a model that can be solved in strict formal analogy to the problem of a bounded two-dimensional quantized oscillator. The doubling of the underlying exponential decay length emerges naturally. One may also extract the underlying direct intermolecular force through which molecular motion is restricted.

Introduction

Ever since the seminal work of Onsager[1] on the packing of stiff rods into ordered structures, it has been known that purely repulsive forces can act to create condensed assemblies of particles. The entropic consequences of steric repulsion have come to be a popular topic in statistical mechanics. The key simplifying feature of virtually all theories has been the assumption that the continuously variable repulsive force between rods can be replaced by that of a hard cylinder whose radius of sudden repulsion depends on the strength of the actual force (see, e.g., the discussion of Stigter[2]).

Recent simultaneous measurements of the molecular disorder of and the forces between polyelectrolytes in parallel arrays[3] suggest that this hard particle assumption is incorrect. For the specific system observed, parallel double helices of polyelectrolyte DNA, one sees two regimes of repulsion:

At separations less than 10 Å, molecules repel with an exponentially decaying force whose decay constant is about 3 Å and is negligibly dependent on salt concentration, as expected for hydration forces;[4] repulsion is so powerful that it suppresses energetically significant molecular disorder.

At greater separations, one observes the onset of molecular disorder and an exponentially decaying intermolecular force whose decay rate depends on salt concentration but is approximately one-half that expected from the standard double-layer theory.

Indeed, this extended decay is the key to the model that we develop here to explain molecular packing. Steric repulsion within an array of parallel flexible rods varies as a power of separation, R,[5–7] quite different from what is observed. The only effect of the underlying soft (e.g., electrostatic) potentials is to change the effective separation.[2] This assumption is again not substantiated by the observed forces.

To develop a better description of the observations, we have formulated a Gaussian model of a polymer enclosed in an effective "tube" of its neighbors confined to their main positions. Solution of this model, formally equivalent to a quantized two-dimensional harmonic oscillator held inside fixed circular boundaries, predicts the two experimentally observed regimes—one close in where forces are just those that act directly between molecules and a second one with appreciable molecular disorder, where forces decay exponentially at half the rate of the underlying direct force.

The length of the Gaussian polymer steps, a priori unknown for a free flight chain, is found to be $\cong$40 Å when the model is fit to measured values. This step length is essentially the same as the 45-Å length of the independently fluctuating unit length previously inferred thermodynamically from correlation of measured lateral fluctuations and osmotic compressibilities. It is also close to the "deflection" length introduced by Odijk[5–7] to describe

---

[*] To whom correspondence should be addressed.

[†] On leave from J. Stefan Institute, P.O.B. 100, YU, 61111 Ljubljana, Yugoslavia.