by Takayanagi,[23] that when internal motion commences, the crystal becomes viscoelastic and can undergo orientational changes more easily. In this way, the onset of internal motion is reflected in the increase in the dynamic orientation function with temperature.

It is desirable, in order to obtain better comparison with dynamic mechanical spectra, to determine the variation of the dynamic orientation function (as determined by X-ray diffraction) with temperature at a fixed frequency and to compare this result with the corresponding variation of dynamic birefringence and modulus. Such studies are presently in progress.

An Entropic Repulsion Theory for Random Copolymer Dispersant Action[1]

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ABSTRACT: An entropic repulsion theory is applied to random copolymer dispersants, where the possibility exists of adsorption of the macromolecule in a flattened conformation. To do this a computer program has been devised which simulates the movements of adsorbed model macromolecules as they undergo Brownian motion with progressive attachment of polar groups to the adsorbing surface. The implications of the configurational behavior results with respect to the dispersancy performance have been calculated.

A recent quantitative theory of polymeric dispersant action[2] considers that the repulsion necessary to prevent particle adhesion arises from the reduction in configurational entropy of the adsorbed polymer molecules when they are compressed on close approach of the dispersant-covered surfaces. The theory was developed in detail for the terminally adsorbed, block copolymer type of dispersant which is the simplest to treat theoretically, since it remains unequivocally in randomly coiled configuration on the surface.

In the present work this theoretical treatment has been extended to cover the more complex case of the random copolymer type of dispersant where, because of the polar adsorbing units distributed at random along the length of the polymer chain, the possibility exists that the adsorbed macromolecule could tend to settle down flat on the surface with progressive attachment of these polar units, rather than retain its original coiled configuration. It is important that the treatment of such changes in adsorbed configuration should be able to take into account the realistic possibility that a polymer molecule, arriving at the adsorbing surface in its coiled "solution configuration," could be greatly hindered in its progress to the thermodynamic equilibrium state of a flattened configuration with virtually every polar group adsorbed, and may well achieve a metastable thick film state. One may readily visualize that this could happen because of appreciable loss of freedom of the polymer chain as soon as some of its polar units are strongly adsorbed, because of entanglement of the adsorbed polymer chain with itself and, at the higher surface coverages, because of entanglement with a neighboring adsorbed chain. Any examination of this possibility by an extension of existing theoretical treatments of such polymer adsorption appeared to be out of the question, since they employ analytic techniques which cannot as yet deal satisfactorily with the self-avoiding random walk problem involved here. A direct computer simulation of the adsorption process seemed most practicable, in which the adsorption of macromolecules of different structure would be followed, and their height, number of adsorbed units, and other quantities of interest would be recorded at intervals. Thus a computer program was devised which simulates the movements of model random copolymer molecules as they arrive at an adsorbing surface, undergo Brownian motion and progressive attachment of polar groups, and approach a limiting adsorbed film thickness. The implications of the configurational behavior differences with respect to the resulting dispersancy performance of random copolymers were then calculated. In this work, it was evident that the number of samples that would be obtained in any reasonable time would hardly be sufficient to give a high degree of precision to the results. Even the generation of random walks with a computer is a relatively lengthy process, and here the generation of a random walk is merely the preliminary to a much longer operation. The work was thus expected to provide broad indications, rather than to show up any statistically significant differences in configurational behavior associated with small changes in conditions.

Method

Outline of Computer Simulation of Adsorbed Behavior. A nonintersecting random chain with 90° bond angles is generated on a simple cubic lattice.[2b] It may be of any length up to 1024 chain elements and polar groups may be introduced, either regularly at specified intervals or at random with a specified average frequency;

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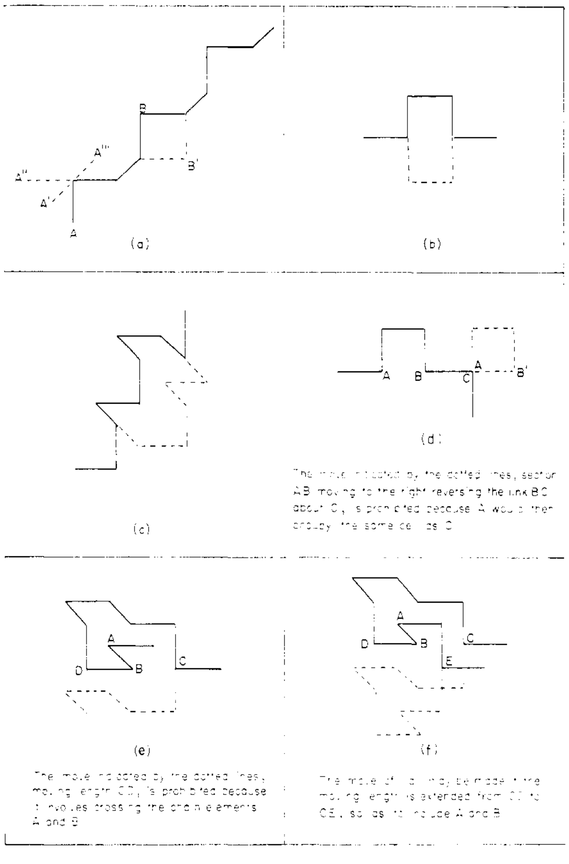
(1) Paper presented at the Colloid and Surface Chemistry Symposium, 154th National Meeting of The American Chemical Society, Chicago, Ill., Sept 10–15, 1967.

(2) (a) E. J. Clayfield and E. C. Lumb, *J. Colloid Sci.*, **22**, 269 (1966); (b) *ibid.*, **22**, 285 (1966).



(d) The move indicated by the dotted lines, sector AB moving to the right reversing the link BC about C, is prohibited because A would then occupy the same cell as C

(e) The move indicated by the dotted lines, moving length CD, is prohibited because it involves crossing the chain elements A and B

(f) The move of (e) may be made if the moving length is extended from CD to CE, so as to include A and B

Figure 1. Model Brownian movements.

only the regular spacing was used in the work reported here. The chain is brought into contact with a surface on which are placed adsorbing sites at specified regular intervals; the height (initial film thickness) and the two widths of the chain are measured, and the numbers of adsorbed polar groups (polar groups at adsorbing sites) and of chain elements in the surface are counted.

The chain then undergoes simulated Brownian (thermal) motion. Here a possible method would be to adopt the Verdier and Stockmayer[3] model of thermal motion, recently used by Bluestone and Cronan[4] in a simulation of adsorption, which is simple to program. This model starts with fully stretched chains with a 90° bond angle on a simple cubic lattice, and simulates thermal motion by selecting chain elements at random; chain ends are moved through 90° from A to A′, A″, or A‴ as in Figure 1a, and other elements from B to B′, with the possible introduction of a 180° bond angle. However, this model has the unrealistic feature that a chain cannot increase its adsorption other than at the ends or by extension of a section already adsorbed; this limitation would be more serious in the present work where adhesion is by adsorption only, than in the model of Bluestone and Cronan where the attraction extends to several bond lengths from the surface.

Consequently, the following method of simulating Brownian motion was devised. A chain element and one of the six directions in the planes of the lattice are selected at random. An attempt is made to move an appropriate segment of chain two lattice units in the selected direction; this segment may be terminated at each end either by an end of the chain, which also moves, or by a link which lies in such a direction that it may be reversed to maintain continuity (Figures 1b and 1c). A chain element is prevented from moving, and hence forbids the movement of the whole segment, if it would pass outside the lattice or below the adsorbing surface. Four sizes of lattice are available, simulating different degrees of packing of molecules on the surface. If the chain element is an adsorbed polar group, it is allowed a preset probability of desorbing or a preset probability, which may be different, of migrating along the surface. A segment containing several such groups is thus unlikely to move if this individual probability is appreciably less than unity. A chain element is prohibited from moving if its destination is occupied (Figure 1d), or if it would cross another part of the chain on the way (Figure 1e); if the threatening chain elements are part of the moving segment, they do not interfere (Figure 1f). To avoid moving the whole chain at once, a moving segment may not extend more than a preset number of elements in each direction from the chain element first selected; the maximum movable length thus allowed was 17 elements.

After a specified number of moves the chain is again measured, and the number of adsorbed polar groups and chain elements in the surface counted. Further Brownian motion continues until either (a) the chain desorbs (no chain elements in the surface), (b) a specified number of unsuccessful attempts (*e.g.*, >1000 for 128-element chains) at Brownian motion are made consecutively (with a suitably large chosen number, this implies that the chain is effectively immovable), or (c) the chain ceases to decrease in height, as shown by the difference between two running means of height at specified intervals. After a, b, or c, appropriate printing occurs and a new chain is generated or fresh data are read.

The program also calculated the statistical weight of the chain so as to allow for the difference between the probability of generating a given chain and of finding a real chain of the same configuration. However, the numbers of chains sampled proved to be insufficiently large to allow these weightings to be used reliably, and in all the results given here each chain is assigned an equal weight.

A form of grouping of Brownian movements is employed to increase the rate of settling down. It seemed likely that if a mild degree of up-and-down oscillation (concertina motion) were applied to the molecule, the rate of adsorption should be increased without seriously affecting the process in any other way. At the start of thermal motion, therefore, any upward movement required by the random number sequence is converted into a downward movement; this continues either until a given number of downward movements have been made (the number is selected by trial), or until a further chain element enters the surface, whichever happens first. An equal number of the opposite moves is then made, and the process starts afresh. This concertina motion doubles the rate of settling.

In the work reported here, no account is taken of

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(3) P. H. Verdier and W. H. Stockmayer, *J. Chem. Phys.*, **36**, 227 (1962).

(4) S. Bluestone and C. L. Cronan, *J. Phys. Chem.*, **70**, 306 (1966).

solvent effects, *i.e.*, the macromolecules are considered as being in a good solvent.

The program was written for an I.C.T. Pegasus digital computer, in the machine language. Approximate calculations regarding the real time scale for the model Brownian movements show that the program conveniently allows up to the first minute or so of the adsorption process of typical dispersant polymer molecules to be simulated. The set probability of desorption of a polar group may be related approximately to a corresponding adsorption energy by considering that only a calculable proportion of individual Brownian movements will be sufficiently energetic to bring about desorption. If a Maxwell energy distribution is assumed, numerically at 300°K the most frequently used probabilities of desorption, 1/1024, 1/32, 1/4, 1/2, respectively, correspond to adsorption energies of 4.2, 2.1, 0.83, 0.42 kcal/mol. Since adsorption from solution is necessarily concerned, such energies are excesses over the adsorption energy of solvent.

Definitions. The height and two widths of a chain are defined in terms of the smallest rectangular box, with axes parallel to the lattice, which just contains the chain. The area occupied by a chain on the surface is defined as the projected area of the containing box, *i.e.*, the product of the two widths.

Unit coverage (surface coverage $\theta = 1$) is defined so that a chain thus adsorbed has available to it an area of surface equal to the mean square of the solution diameter. It is possible for strong adsorption to give a close packing with a high degree of lateral compression and $\theta > 1$. If the solution diameter of 128 link chains is taken[2b] to be 12 units, the coverages studied are approximately 0.14, 0.56 and 2.24, referred to as low, intermediate, and high, respectively.

An abbreviated notation for chain conditions is used in which, for example, 4-1/32-32 denotes a chain in which one chain element in 4 is a polar group, one surface site in 1 (*i.e.*, every site) is an adsorbing site, the probability is one in 32 that a single adsorbed polar group can leave the surface at a single attempted movement, and one in 32 that it can migrate along the surface.

Results and Discussion

The characteristic types of adsorbed macromolecule behavior met in this study may be conveniently classified in terms of height variation. Here the total height of the molecule has been regarded as the important parameter, rather than a mean height obtained from the density distribution, since it is this total height that is believed[2a] to determine the dispersancy behavior of the polymer.

Most of the simulated polymer molecules fluctuate in height. Nonflattening molecules in this category behave as shown in Figure 2a. The amplitude of fluctuation depends on the type of molecule and is irregular, but it may amount to half the total height of the molecule. This fluctuation is of much lower frequency than the concertina motion intentionally applied to increase the rate of the adsorption process, and is probably akin to the reported[3,5] oscillations of end-to-end distance of simulated free polymer chains. In contrast, some nonflattening molecules rapidly achieve a metastable thick film state in which little or no height fluctuation occurs (Figure 2b).

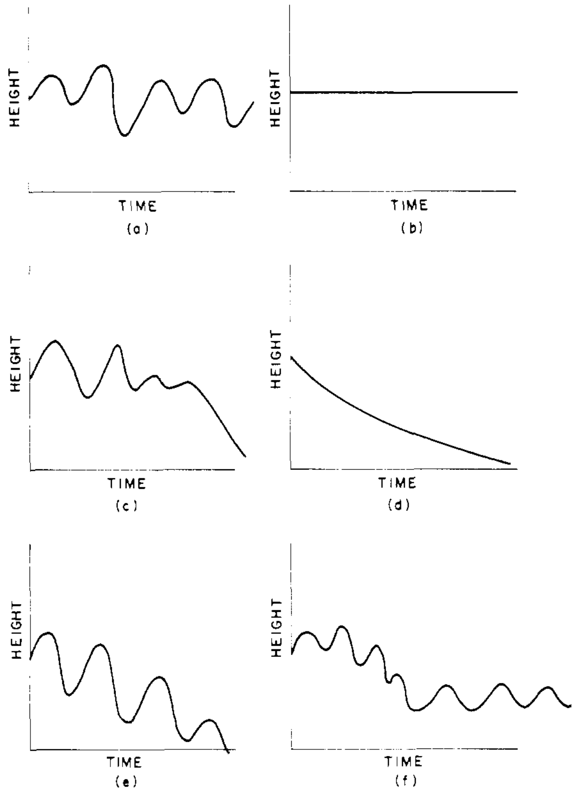

Figure 2. Characteristic types of height variation of adsorbed chains.

Simulated molecules which adsorb flat onto the surface do not do so immediately; they exhibit an "induction period" during which they fluctuate in height for some time, and then collapse rather suddenly onto the surface (Figure 2c). A consequence of this is that a good deal of the initial work was carried out with too short a period of observation to detect flattening of some molecules ("short runs" up to 3000–4000 movements). The work done after this was at the extreme of practicable computing times ("long runs" up to 16,000 movements), and is necessarily more limited in the number of samples examined. The applicable parts of the short runs were used to supplement the results with a greater variety of molecular type and conditions, and with a greater degree of replication.

Types of height variation which were not found to be characteristic of particular sets of conditions, though occasionally observable in single molecules, are the steady decrease (Figures 2d and 2e) and a drop to some value intermediate between solution diameter and substantially complete flattening (Figure 2f).

The influence of surface coverage on chain flattening is shown by the results given in Table I. Here the program was modified in two respects, in order to make the best use of computing time. When the running mean height of the chain dropped below four units a fresh chain was started; *i.e.*, a height of less than four units was regarded as a sufficient approach to flatness for present purposes. For 128-element chains, only those with an initial height greater than the mean, *i.e.*,

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(5) S. Bluestone and M. J. Vold, *J. Chem. Phys.*, **42**, 4175 (1965).

TABLE I
INFLUENCE OF SURFACE COVERAGE ON CHAIN FLATTENING

No. of elements in chains	Chain conditions	Area of lattice	θ	No. of chains examined	No. of chains flattening	Mean initial height of chains	Mean height of non-flattening chains	Percentage of polar groups adsorbed
128	1-1/1024-1	32 × 32	0.14	8	8	14	...	84
		16 × 16	0.56	2	2		...	88
		8 × 8	2.24	3	0		10.6	32
	1-1/4-4	32 × 32	0.14	6	5		14.0	91[a]
		8 × 8	2.24	2	0		13.0	34
512	1-1/1024-1	32 × 32	0.56	3	0	22	24.6	29
		16 × 16	2.24	2	0		21.6	33

[a] Mean value for the five chains which flatten.

Figure 3. Typical configuration of a flattened chain. Condition 1-1/1024-1, 128 elements, θ = 0.14.

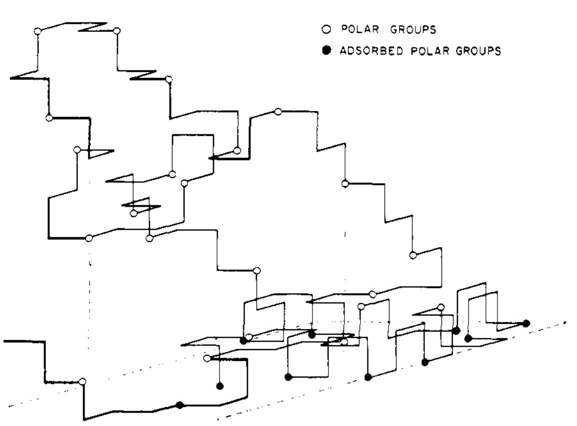

Figure 4. Typical configuration of a nonflattening chain at low coverage. Condition 4-1/4-4, 128 elements, θ = 0.14.

$\geqslant$12 units, were used; this selection enabled the tendency to flatten to be detected with greater certainty.

The results for chains of 128 elements indicate that chains which flatten at low surface coverages are prevented from doing so as surface coverage is increased. Every chain in condition 1-1/1024-1, and all but one of 1-1/4-4 flattened at low θ, and 1-1/1024-1 settled similarly at intermediate θ. At high θ, however, little or no flattening occurred, the chains retaining a mean height approximating to their original solution diameter. Condition 1-1/1024-1 represents a strongly adsorbing molecule with complete surface mobility, 1-1/4-4 a much weaker adsorption, though with no more surface mobility than the rather ready desorption allows. The chains of 512 elements, in condition 1-1/1024-1, show no signs of flattening at either high or intermediate θ; a large enough lattice was not available to simulate low θ. The differing behavior of the two chain lengths at intermediate θ could be a genuine effect of chain length, or may arise from the possibility that the time required for the longer chain to settle exceeds the computer time available (~16,000 movements).

It is noteworthy that in flat adsorption nearly all the polar groups are bound to the surface; otherwise about a third are bound, in the case of nonflattening chains. It would seem that a bound fraction of a third or so does not necessarily denote a flattened adsorbed configuration, as assumed hitherto,[6,7] but is compatible with an adsorbed film with a thickness comparable to the solution diameter. Typical configurations of flattened, and nonflattening, chains produced in this present work are illustrated in Figures 3 and 4, respectively.

Since chains are not observed to flatten at high surface coverage, the strength of adsorption of a macromolecule can influence the adsorbed height only at intermediate and low coverages. The influence of strength of adsorption on adsorbed macromolecule behavior is shown by the results, given in Table II, for chains of 128 links at low θ. Three factors which affect the strength of adsorption of a polymer molecule as a whole are taken into account, namely, the strength of adsorption of individual chain elements, the proportion of chain elements which are adsorbable, and the proportion of surface sites that are adsorbing. In the work reported here the last factor remained unchanged at 100%.

From Table II it can be seen that the smaller the proportion of polar groups in a chain, and the smaller the strength of attachment of individual polar groups to the surface, the smaller is the tendency of the chain to settle down flat but the greater is its tendency to leave the surface, *i.e.*, desorb. A clearer picture of the quantitative relationship between molecular structure and adsorbed behavior may be obtained by taking the product of the fractional frequency of polar groups in the macromolecule and the adsorption energy per polar group as a numerical rating of the strength of adsorption of the macromolecule as a whole, and plotting these results in the form shown in Figure 5. It is apparent from this figure that a quite critical balance of structural properties is necessary if flattening of a random copolymer molecule is to be prevented without causing excessive desorption.

Polymer molecules may be restrained from collapsing onto the surface by two things, therefore—by being

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(6) B. J. Fontana and J. R. Thomas, *J. Phys. Chem.*, **65**, 480 (1961).

(7) C. Thies, *ibid.*, **70**, 3783 (1966).

TABLE II
BEHAVIOR OF ADSORBED CHAINS OF 128 ELEMENTS AT LOW θ

Chain conditions	No. of chains examined	No. of chains leaving surface	No. of flattening chains	No. of non-flattening chains remaining adsorbed	Fractional frequency of polar groups in chain, f	Adsorption energy per polar group, E, kcal/mol	fE
			Long Runs[a]				
1-1/1024-1	8	0	8	0	1.0	4.2	4.2
1-1/4-4	6	0	5	1	1.0	0.83	0.83
4-1/32-32	5	0	4	1	0.25	2.1	0.53
6-1/32-32	6	3	2	1	0.167	2.1	0.35
16-1/1024-1024	12	7	2	3	0.0625	4.2	0.26
4-1/4-4	17	15	0	2	0.25	0.83	0.21
16-1/32-32	19	17	0	2	0.0625	2.1	0.13
			Short Runs				
1-1/2-2	10	1	0	9	1.0	0.42	0.42
4-1/4-4	28	18	0	10	0.25	0.83	0.21
16-1/32-32	25	9	0	16	0.0625	2.1	0.13

[a] Using chains with initial height $\geqslant 12$ units.

insufficiently strongly adsorbed, or by having too little room to move, and, presumably, by combinations of the two in the sense that a moderately strongly adsorbed molecule will be prevented from flattening at a lower coverage than one which is very strongly adsorbed.

A typical history of a molecule that flattens (*i.e.*, type c of Figure 2) is shown in Figure 6. In the early stages the chain fluctuates in height to some degree and meanwhile a number of polar groups are adsorbed. Subsequently the fraction of adsorbed polar groups remains roughly constant while the height fluctuates, and then rises sharply at about the time that the height falls. The fraction adsorbed at this critical point, at the end of the "induction period," is found to be remarkably constant at one-half for the flattening chains examined. It seems likely that the part of the molecule already adsorbed hinders the attachment of the remaining loops until some suitable configuration is attained; the eventual attachment of this relatively small part of the chain may then account for the rather sudden reduction in height. The fraction of polar groups adsorbed on flattening is near unity, and considering that flattening was not allowed to develop to completion in this work, it is evident that practically every polar group may be adsorbed when a chain reaches its final flat form. The configurational behavior before this sudden reduction in height is similar to that exhibited by most nonflattening chains, of the type depicted in Figure 2a, where the fraction of adsorbed polar groups remains roughly constant at about one-third. In contrast, some nonflattening chains, type b of Figure 2, rapidly achieve an essentially incompressible state where very little fluctuation in height occurs. This type of behavior is particularly associated with high surface coverage conditions. A typical history of such a nonflattening chain is given in Figure 7.

When the implications of such configurational behavior differences with respect to the resulting dispersancy performance of random copolymers are considered, it is clear that two types of behavior, complete chain flattening and severe desorption, cannot give effective polymeric dispersant action. Calculations of the dispersancy behavior resulting from the types of configurational behavior which could provide protection against particle adhesion, namely, those where the adsorbed macromolecules maintain a nonflattening state which is either of a rigid or a fluctuating nature, have been carried out using the entropic repulsion theory of dis-

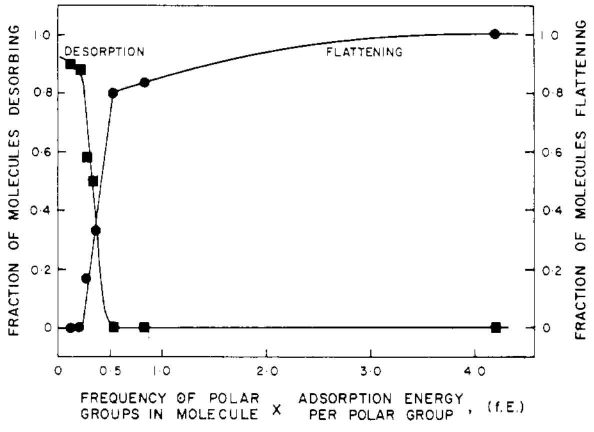

Figure 5. Influence of strength of adsorption on configurational behavior of adsorbed macromolecules, at low surface coverage: 128-element chains; θ = 0.14.

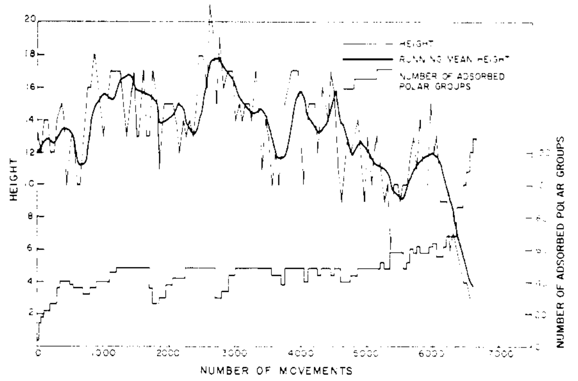

Figure 6. A flattening chain. Condition 1-1/4-4, 128 elements, θ = 0.14.

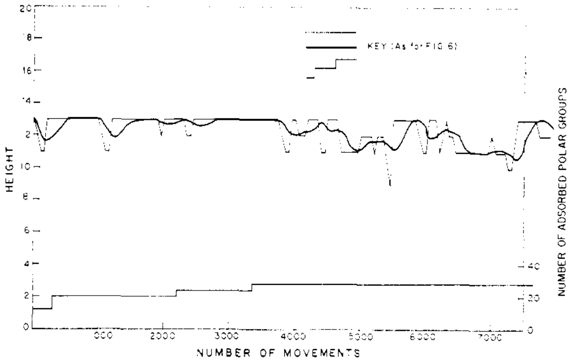

Figure 7. Height fluctuations at high coverage. Condition 1-1/1024-1024, 128 elements, $\theta = 2.24$.

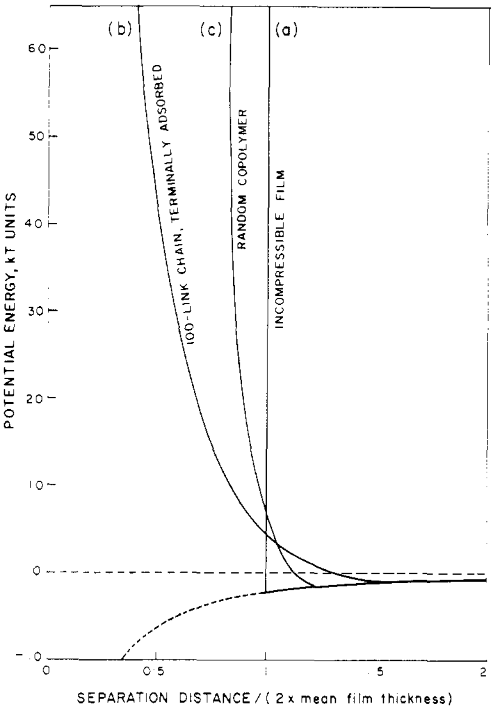

Figure 8. Interaction curves for (a) incompressible film, (b) film of terminally adsorbed chains, (c) film of random copolymer chains, at equal root-mean-square film thicknesses. Sphere/plate interaction, $a/l_r = 5$, $\theta = 1.0$, $A/kT = 12.5$.

persancy.[2a] These calculations are expressed in the usual form of potential energy diagrams (Figure 8), where the resultant interaction energy is obtained as the sum of the entropic repulsion energy (positive) and the attraction energy (negative).

For the entropic repulsion calculations, the model system considered is that of a spherical particle, radius a, separated by a distance H from a plate, with both surfaces coated with adsorbed polymer chains of root-mean-square (rms) height l_r at a surface coverage θ. If pairs of chains of height l_l on opposing surfaces just touch when those on the sphere lie on a circle which subtends, at the center of the sphere, a semiangle ϕ to the perpendicular to the plate, the entropic repulsion V_R for the system is given in kT units by eq 1, where $W(l_l/l_r)$ is the proportion of the total number of configurations of a molecule for which the distance of the extremity of the chain from the adsorbing surface is less than l_l.

$$\frac{V_R}{kT} = 2\pi\theta \int_0^{\pi/2} \frac{(2a/l_r) + (H/2l_r)^2}{(1 + \cos\phi)^2} \times \sin\phi \cos\phi \left[-\ln W\left(\frac{l_l}{l_r}\right) \right] d\theta$$

The following equation was used for the London–van der Waals attraction energy V_A, in kT units, between the spherical particle and the plate, where A is the Hamaker constant. In the calculations A/kT was taken to be 12.5, *i.e.*, $A = 5.05 \times 10^{-13}$ ergs at 20°.

$$V_A = -\frac{A}{6kT}\left[\frac{2a(H + a)}{H(H + 2a)} - \ln\left(\frac{H + 2a}{H}\right)\right]$$

In Figure 8, the resultant interaction energy is plotted as a function of the dimensionless separation distance $H/2l_r$, for three types of polymer molecule. In the entropic theory of dispersancy, the repulsion exerted by an adsorbed molecule when compressed is related to the proportion of the total number of configurations available to it which are excuded as a result of the compression. For an incompressible molecule of fixed height l_r, approximating to the "nonfluctuating" case of Figure 7, the repulsion is thus zero at distances of separation H greater than $2l_r$ since no configurations are then excluded, and infinite at distances less than $2l_r$ (Figure 8, curve a). For comparison, the interaction curve for a fairly flexible terminally adsorbed macromolecule of equal rms height is also shown (Figure 8, curve b). The interaction curve for the type of random copolymer molecule, of equal rms height, which fluctuates in height between fixed limits, corresponding to type a of Figure 2, shows an intermediate degree of repulsion (Figure 8, curve c). The potential energy maximum is very high for the terminally adsorbed macromolecule and infinite for the other two, so that in all three cases irreversible adhesion should be prevented. The minima in the potential energy curves increase arithmetically in the order terminally adsorbed polymer, fluctuating random copolymer, incompressible molecule, and thus the protection afforded against reversible adhesion decreases in the same order. Increase of height of each molecule, with the same attraction constant, increases the protection against adhesion by decreasing the potential energy minimum. An increase of height, however, will generally be achieved only with a corresponding increase in the area occupied by the macromolecule on the adsorbing surface and this will tend to reduce the repulsion.

Thus, random copolymer dispersant molecules will be effective in preventing particle adhesion in proportion to their adsorbed height and in proportion to the degree of fluctuation of height. Indefinite improvement in protection with increase in height will not be possible, however, because at some stage, depending on the size of the protected particles,[2a] too few macromolecules on opposing surfaces will be in contact to exert the required repulsion to prevent irreversible adhesion. Therefore, the dispersant action of random copolymers is expected to improve with decreasing strength of adsorption, subject to sufficient coverage of the surface being maintained.