Orientational effects and ordering of flexible-chain polymers in concentrated solutions and in bulk

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The structure of concentrated polymer solutions in which the stiffness of chains was insufficient for the formation of liquid-crystalline phase but the energy of interaction between units depended on the chain conformation at the contact point was investigated. The energy ϵ_0 was attributed to the parallel arrangement of contacting units and energy ϵ_{def} to the non-parallel 'defect' contacts. Direct Monte Carlo computer simulation was used for self-avoiding chains consisting of $N = 61$ units on a simple cubic lattice under periodic boundary conditions. In highly concentrated solutions the non-equivalence in energy of contacts leads to chain extension accompanied by an increase in the mean length of stiff segment and decrease of chain folding. The overwhelming majority of contacts are always of intermolecular nature. These effects become important only when a considerable difference $\epsilon_{def} - \epsilon_0 \simeq 1 - 2\ kT$ in the energy of parallel and 'defect' contacts exists.

Keywords Flexible-chain polymers; amorphous state; computer simulation; lattice model

INTRODUCTION

The first theoretical analysis of polymer structure in concentrated solutions and in the amorphous state has been undertaken by Flory[1,2] when he established the relationship between the behaviour of macromolecules in concentrated solution and their intramolecular characteristics, i.e., chain flexibility.

According to this theory[1,2], for flexible polymer chains the random-coil state remains favourable from the stand point of entropy up to maximum concentrations corresponding to the polymer in bulk (although the entropy of each chain decreases with increasing concentration). In contrast, for stiffer chains the increase in concentration renders the disordered state thermodynamically unstable and at a certain concentration C_{lc} a spontaneous transition to the liquid crystalline nematic phase occurs. For chains exhibiting no internal degrees of freedom, i.e., for rigid rods, the concentration C_{lc} is related to the anisotropy parameter P (ratio of the rod length to its diameter) by the equation:

$$C_{lc} \simeq \frac{8}{P}\left(1 - \frac{2}{P}\right) \qquad (1)$$

At $P < P_{min} = 6.4$–6.7[2,3] the system of rods can remain disordered at any concentrations. For long semi-rigid chains containing a large amount of segments with average length P the condition for maintenance of a disordered structure in the absence of solvent is given by:

$$f > f_{min} = 1 - \frac{1}{e} \simeq 0.63 \qquad (2)$$

or by the equivalent condition:

$$-\frac{\varphi_{segm}}{PkT} > \left(-\frac{\varphi_{segm}}{PkT}\right)_{min} = 1 \qquad (2')$$

where φ_{segm} is the conformational free energy of a rigid chain segment in a dilute solution and $f \sim 1/P$ is the flexibility parameter: the fraction of rotational isomers distorting the stiff chain structure. In the disordered state the macromolecules retain the same flexibility as in a dilute solution and they extend when the liquid-crystalline phase is formed.

The present paper is concerned with the effect of interchain interaction on the structure of macromolecules in concentrated polymer solutions. Its main purpose is to analyse the possibility of ordering for polymers in which the stiffness of their chains is definitely insufficient for the formation of an ordered structure: $f > f_{min}$. It will be shown that the generation of order due to the effect of interchain interactions is possible when the interaction between units depends on the mutual orientation of units, and on the chain conformation at the contact point.

Computer simulation methods for a lattice model of concentrated polymer solutions are used. Below we shall discuss the result of computer simulation for systems in which the segment–segment interactions are not orientationally dependent. Then the importance of orientational effects will be shown. Models and their reference to real systems will be discussed.

SIMULATION AND RESULTS

Simulation of the structure of amorphous polymers

At present many experimental data have been obtained showing that the macromolecules in amorphous polymers have the shape of Gaussian coils in complete

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agreement with Flory's model[3-5]. The investigations of polystyrene, polymethylmethacrylate, polyethylene and other flexible-chain polymers in the melt, in concentrated solutions and in bulk, carried out by neutron and X-ray scattering[6-8] from labelled molecules have shown that their dimensions coincide with those of chains in dilute θ-solutions and the shape of the scattering curve coincides with that of the theoretical curve for Gaussian coils[8-10]. In individual chains the Gaussian structure is compatible with the existence of a short-range one-dimensional order within a single segment[11,12]. Similarly, regions exhibiting a short-range three-dimensional order, close in size to that of a chain segment, have been revealed in amorphous polymers[13-16].

Recently, direct Monte Carlo computer simulation has been widely used for the analysis of the structure of concentrated polymer solutions[18-27]. These works considered a lattice model for polymer solutions which also provides the basis of analytical theories. However, in contrast to the latter in which definite approximations are always used (in particular, the mean field approximation[1,2], which is not rigorous as is indicated in ref 17), computer simulation[18-27] takes into account the strict statistics of the system considered.

Systems of flexible self-avoiding chains random walking on cubic or tetrahedral lattices were investigated. The contact between any pair of units of the same macromolecule or different macromolecules was characterized by contact energy ε. The lattice cells free of the polymer were assumed to be occupied by the solvent. Chains in the athermic solvent, $\varepsilon=0$ with number of segments $N=6$–30, have been considered in refs 18–23. The maximum degree of space filling with polymer chains (volume concentration of the polymer in the system) was as high at 0.9–0.95[22,23]. The effect of solvent strength was investigated in refs 24–27. Solvent strength has been determined by the value of contact energy ε over the range $-0.5\leqslant-\varepsilon\leqslant 0.5$ where ε is measured in kT units[24-27]. The value of ε is the difference effect due to the replacement of polymer–solvent contacts with polymer–polymer contacts. It is related to the analogous Flory's parameter χ[28] by the equation $-\varepsilon=2\chi/z$ where z is the coordination number of the lattice.

The most detailed investigations of the concentration behaviour of a model flexible-chain system have also been carried out in refs 24–26. Concentration dependences of size (mean-square end-to-end dimensions and mean-square radii of gyration), average numbers of inter- and intramolecular contacts, mutual arrangement and mean lengths of contacting chain parts etc. have been analysed.

On average, the results of all works on the modelling of concentrated solutions and the amorphous state of polymers are in good agreement. These results are as follows:

(1) When polymer concentration increases both the total size of the chains and all detailed characteristics of their microstructure tend to θ-values.

(2) The tendency of the chain to reach the θ-state at increasing concentration in solvents of different strengths appears beginning with low polymer concentrations and essentially disappears when the solvent is still present in amounts of not less than 50%.

(3) Mutual chain arrangement in a highly concentrated state is entirely chaotic: the fraction of parallel units located side by side corresponds to the statistics of random contacts and the absence of any correlation in the mutual arrangement of chain parts. Moreover, the statistics of random contacts in itself leads to the appearance of some amount of parallel fragments from one or two segments, being intra- or intermolecular in nature.

Figure 1 shows, as an example, the concentration dependences of the mean-square end-to-end dimensions and the average number of intra- and intermolecular contacts (normalized for their limiting value) for a flexible chain consisting of $N=61$ units on a cubic lattice[24]. The number of contacts determines the local density of units near an arbitrary chain unit. The cases of a good (athermal) solvent $\varepsilon=0$, an ideal θ-solvent, $-\varepsilon=-\varepsilon_\theta=0.3$[29,30] and a precipitant, $-\varepsilon=0.5$ are shown.

It is emphasized that these results should not be regarded as evidence of complete disorder in amorphous polymers. They show that the increase in polymer concentration in this system does not lead to additional intramolecular ordering. The extent of a short-range one-dimensional order existing in isolated chains and determined by the segment length does not vary with concentration. It follows from point (3) that the segment length also determines the size of regions of transverse order.

Model for a system with orientation-dependent interactions between units

The important feature of the above described model for a polymer solution that has not yet been considered in detail is the assumption that the energy of contacting units is identical regardless of their mutual orientation and chain conformation at the contact point. The identical value of ε (in particular $\varepsilon=0$, as in refs 18–23) was ascribed to all types of contacts shown in *Figure 2*.

However, in real polymer systems one can expect contacts between units oriented parallel to each other to be more favourable owing to the existence of the special direction along the chain. Presumably, the non-parallel chain fragments or bends at the contact point weaken the contact making it less favourable energetically.

To investigate the effect of the non-equivalence of different contacts the energy ε_0 will be attributed to the parallel arrangement of contacting units and energy $\varepsilon_{\text{def}}=\varepsilon_0+\Delta\varepsilon$ (*Figure 2*) will be attributed to non-parallel 'defect' contact. For simplicity, in our calculations the energies of any non-parallel 'defect' contacts were assumed to be identical. The value of ε_{def} was varied from 0 to 5, which corresponds to the increasing disadvantage of non-parallel contacts as compared to the polymer–solvent contacts (empty lattice cells correspond to the solvent). The energetic interaction between units coming into a parallel contact was taken to be $\varepsilon_0=0$, -0.3 and -0.5.

It was found that the dependence of our results on the value of ε_0 is apparent mostly at low polymer concentrations and this dependence is similar to that obtained for the case $\varepsilon_{\text{def}}=\varepsilon_0$ (*Figure 1*). At high polymer concentrations when the number of chain–solvent contacts becomes small, the properties of system are mainly affected by the relative advantage of $\Delta\varepsilon=\varepsilon_{\text{def}}-\varepsilon_0$ of parallel and 'defect' contacts rather than by the values of ε_0 and ε_{def} separately.

All calculations were carried out for self-avoiding

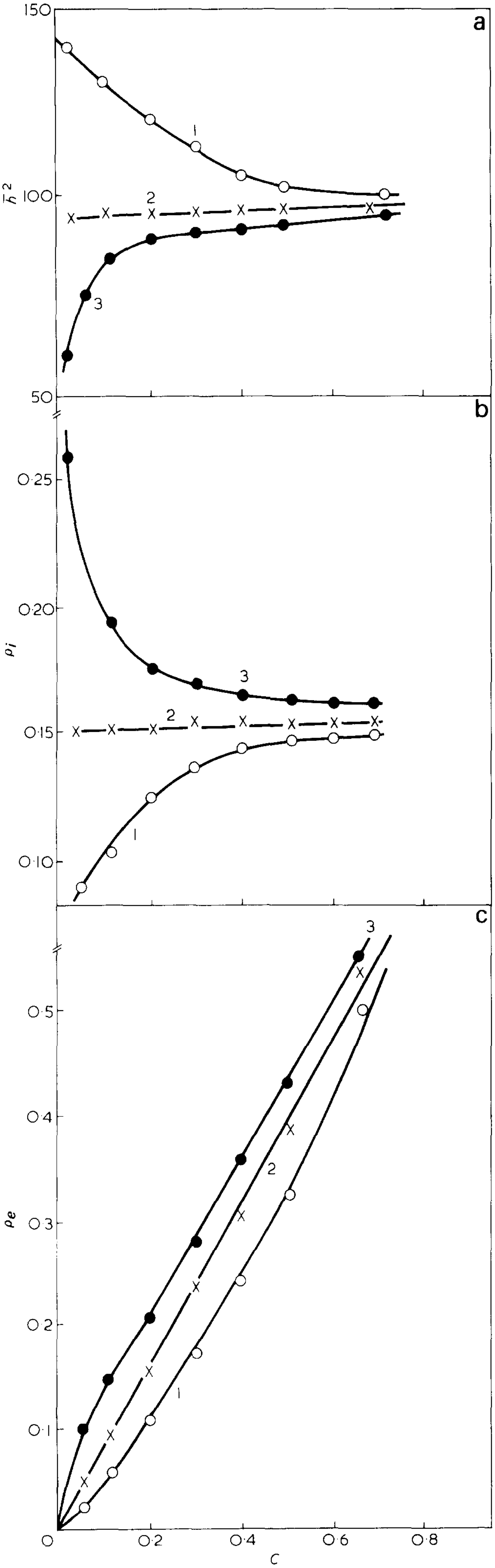


Figure 1 (a) Mean-square end-to-end dimensions $\overline{h^2}$; (b) intramolecular local density of segments ρ_i, equation (3); (c) intermolecular local density of segments ρ_e, equation (3'), all vs. the volume concentration C of polymer in solution, for various values of the parameter $-\epsilon_0 = 0$ (curves 1); 0.3 (curves 2); 0.5 (curves 3); $\Delta\epsilon = 0$

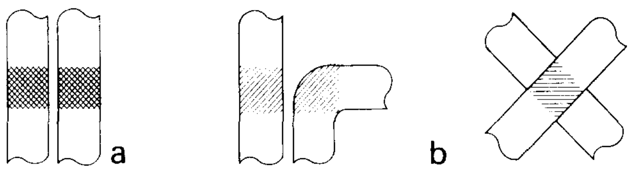


Figure 2 Model representation of (a) favourable contact (energy ϵ_0) and (b) unfavourable contacts (energy $\epsilon_0 + \Delta\epsilon$, $\Delta\epsilon \geqslant 0$)

chains consisting of $N = 61$ units on a simple cubic lattice with equal probabilities of steps in all five directions. The chains were generated one after another inside a cube under periodic boundary conditions up to the given degree of cube filling c. The length of the cube side L was 17 at $C < 0.5$ (up to 40 chains in the cube) and $L = 11$ at $C > 0.5$. The origin of each chain was chosen in a random way and units were generated successively by random chain propagation to the free lattice cells using Rosenbluth's method[31]. To avoid the danger of an 'impasse' situation (when a growing chain enters an impasse this filling of the cube should be discarded) additional procedure of enrichment was used. It was assumed that for each n chain units ($n = 10$) a 'branch point' exists where in principle K independent attempts at chain generation can be made ($K = 10$). The filling of space was considered inadequate and was discarded only if all K attempts to generate the chain ended in an impasse.

Moreover, since preliminary evaluation has shown that at $\Delta\varepsilon \neq 0$ it is possible to expect stiffening of chains, the ensemble of various fillings of the cube with chains was enriched with several subensembles of semi-rigid chains (compare with ref 32). Each subensemble consisted of $\sim 10^2$ fillings of the cube with chains of the same rigidity (each chain was generated similar to the procedure described in ref 33) and the mean length of a rigid segment in subensembles was varied from 1.5 to 7.

For a correct averaging of the characteristics of the system the statistical weight of each given degree of cube filling was characterized by the following factors:

(1) Rosenbluth factor[31] taking into account the selection of only free cells.

(2) Factor $1/K$ ascribed to each 'branch point' and taking into account the chain enrichment.

(3) Factor $\exp[-m_1(\varepsilon_0 + \Delta\varepsilon) - m_2\varepsilon_0]$ taking into account the energy of a given state where m_2 and m_1 are the numbers of 'favourable' and 'unfavourable' contacts in a given configuration (given cube filling).

(4) Factor taking into account the probability of a random appearance in the simulated system of a system of chains corresponding to a given term in the subensemble (for further details see ref 32).

The total number of cube fillings was $(2–3) \times 10^3$. The results were controlled by comparing the data of independent generations, and moreover, the number and parameters of subensembles were varied. All the results were reliably reproduced at $C \leqslant 0.5$. At $C \sim 0.7–0.8$ and high values of $\Delta\varepsilon$ the scattering of data increases and only the general tupe of dependences can be determined.

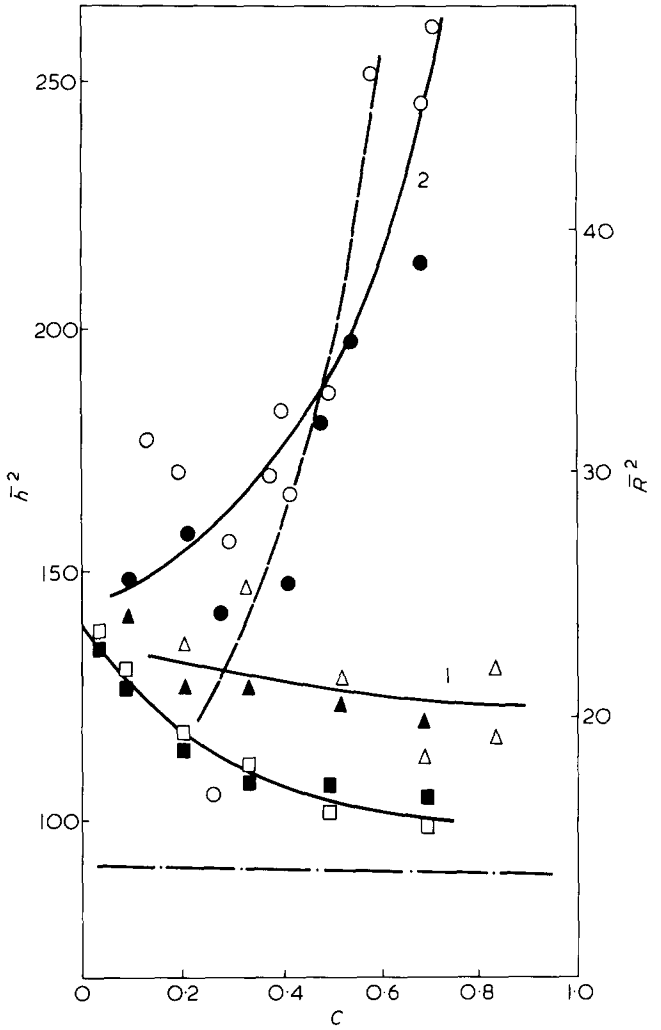


Figure 3 Mean-square end-to-end dimension $\overline{h^2}$ (open symbols and mean-square radius of gyration $\overline{R^2}$ (filled symbols) vs. concentration C for $\epsilon_0 = 0$ and various values of the parameter $\Delta\epsilon$ (numbers at the curves). Dot-dashed line represents the value of unperturbed chain dimensions, dashed line gives the results obtained from equation (5) for $\Delta\epsilon = 2$

Results of computer simulation for a system with orientation-dependent interactions

Figures 3–7 show results of computer simulation for the above described model. All the results except those shown in *Figures 5b* and *c* are given for good solvent ($\varepsilon_0 = 0$) since the decrease of the solvent strength over the range of ε_0 investigated (up to $\varepsilon_0 = -0.5$) does not change the qualitative character of dependences (*Figures 5b* and *c*).

Figure 3 shows concentration dependences of chain dimensions: mean-square end-to-end dimensions and mean-square radii of gyration. Curve '0' represents the data in refs 24–26 for a 'good' solvent in the absence of orientational effects ($\varepsilon_{\text{def}} = \varepsilon_0 = 0$) and curves 1 and 2 characterize the increasing orientational effects.

It can be seen in *Figure 3* that in a dilute solution ($C \sim 0$) orientational effects have little influence on chain size whereas at high concentrations and high values of $\Delta\varepsilon$ the chain size increases with concentration, i.e., the macromolecules extend.

Figure 4a shows the concentration dependence of the mean length of a stiff chain part between neighbouring bends (*gauche* isomers). Chain extension occurring at high $\Delta\varepsilon$ is connected with increasing chain stiffness, i.e., with the extention of the short-order regions in macromolecules.

In the absence of orientational effects (at low $\Delta\varepsilon$) the chains retain the initial flexibility over the entire concentration range. It is known[17,28] that in this case the change in the chain size with concentration is related to the elimination of a long range volume interaction and to the rearrangement from the state of swollen coils to the Gaussian conformation. *Figure 4a* also shows that in a dilute solution chain stiffness as well as chain size are only slightly dependent on $\Delta\varepsilon$.

Figures 5 and *6* show the influence of orientation effects on local chain characteristics: the average number of intramolecular, $\bar{m}_i$, and intermolecular, $\bar{m}_e$, contacts determining the local density of this chain's and other chains' units in the first coordination sphere near the chain

$$\rho_i = 2\bar{m}_i/(z-2)N = \bar{m}_i/2N \qquad (3)$$

$$\rho_e = 2\bar{m}_e/(z-2)N = \bar{m}_e/2N \qquad (3')$$

The orientation effects causing chain extension and stiffening decrease the number of intramolecular contacts. In contrast, the number of intermolecular contacts increases under the influence of orientational effects and as a result the total number of contacts of a chain (or a single unit) is dependent only on polymer concentration (*Figure 7*).

The influence of orientational effects on the mean length of contacting chain part (parts coming into uninterrupted contact with parts of its own chain or other

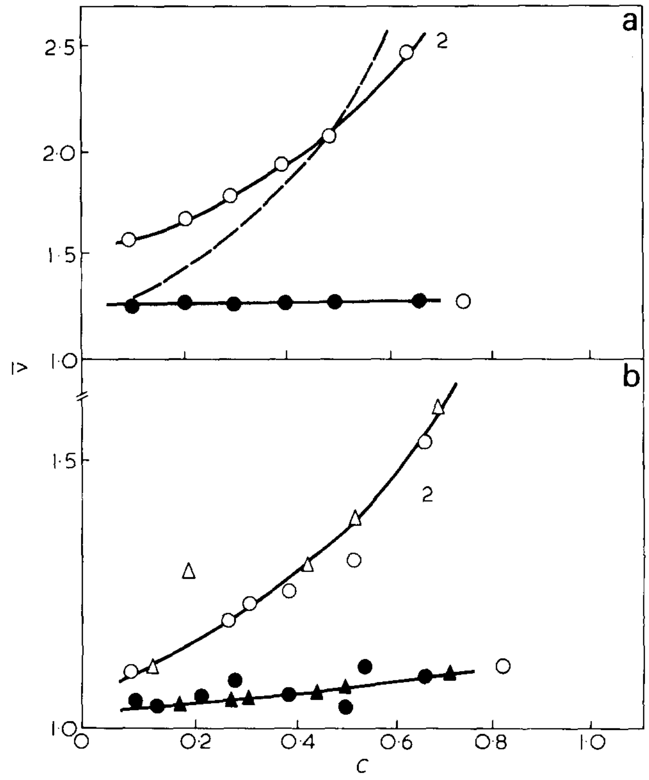
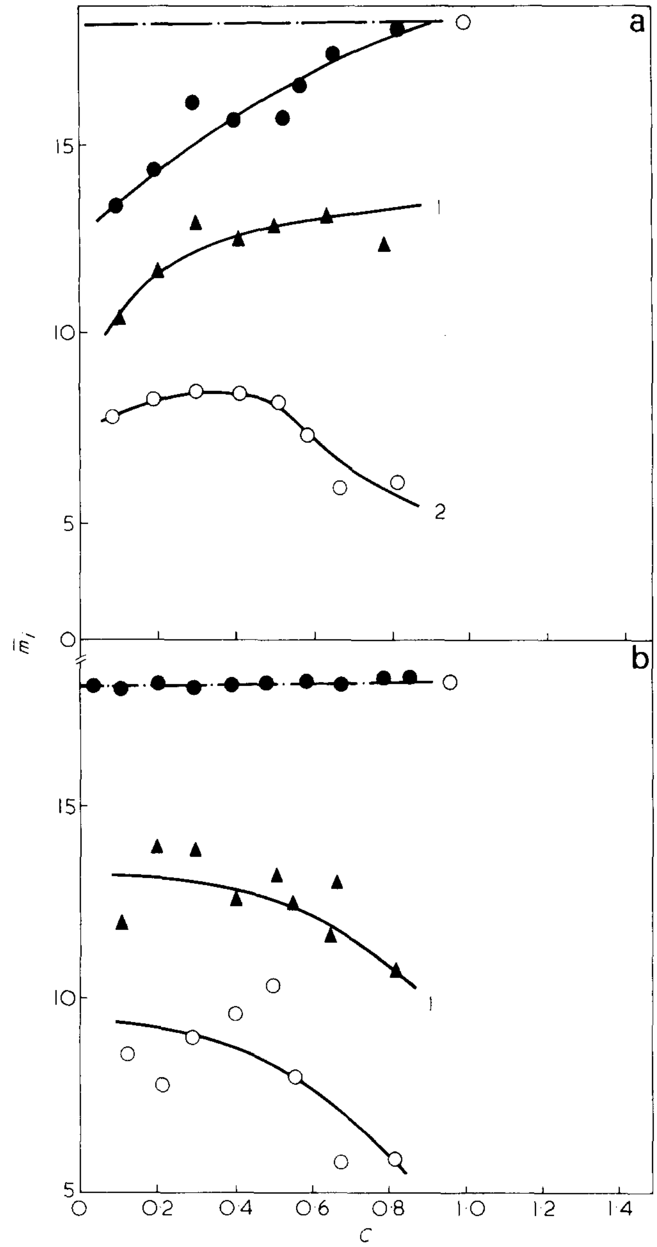


Figure 4 Mean length of (a) stiff segments $\bar{\nu}$ and (b) contacting ones $\bar{\nu}_c$ (△, ▲ intramolecular contacts; ○, ● intermolecular contacts) vs. the concentration C for various values of the parameter $\Delta\epsilon$ (numbers at the curves), $\epsilon_0 = 0$. Dashed line gives the results obtained from equation (6) for $\Delta\epsilon = 2$



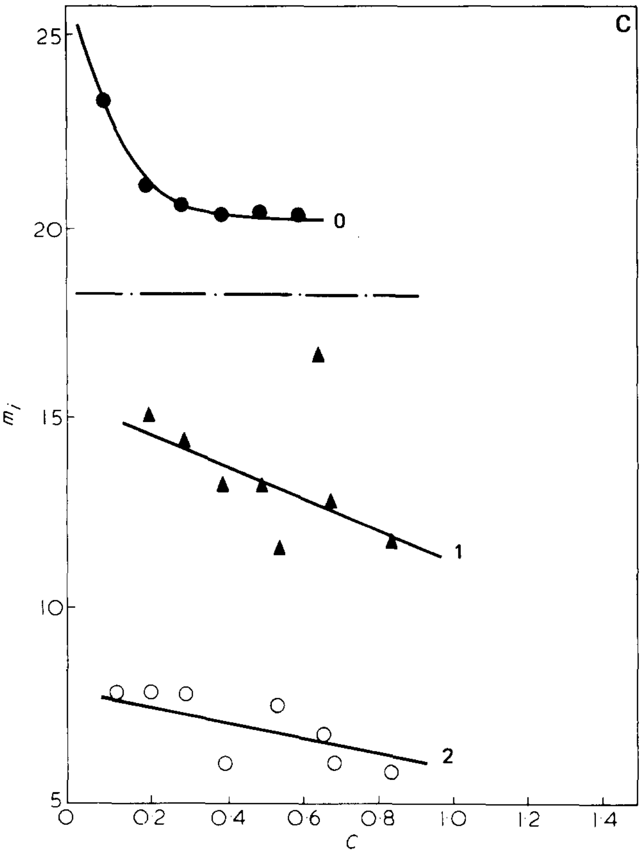


Figure 5 Average number of intramolecular contacts vs. concentration C for various values of the parameters $\Delta\epsilon$ (numbers at the curves) and $\epsilon_0 = 0$ (a); -0.3 (b); -0.5 (c). Dot-dashed lines represent the number of intramolecular contacts in the θ-state

chains) is shown in *Figure 4b*. The mean lengths of fragments with intra- and intermolecular contacts practically coincide. This result is valid for other values characterizing the statistics of intra- and intermolecular contacts (see also *Figure 6*). At $\Delta\varepsilon = 0$ (curve 0) the mean length of the contacting fragment is relatively small and virtually independent of C, i.e., the statistics of random contacts is valid over the entire range investigated[26]. Orientational effects lead to the increasing length of the contacting chain fragments. The higher the concentration and the $\Delta\varepsilon$ value, the longer the length.

Figure 6a shows the contribution of intermolecular contacts to the total number of contacts at different $\Delta\varepsilon$ values as a function of concentration. The fraction of intermolecular contacts increases markedly with concentration so that at high concentrations the majority of contacts are intermolecular. It should be noted that as the orientation effects ($\Delta\varepsilon$) increase, the contribution of intermolecular contacts to the total number of contacts also increases.

Figure 6b shows the fractions of undefected (parallel) intramolecular $\bar{m}_{i0}/\bar{m}_i$ and intermolecular $\bar{m}_{e0}/\bar{m}_e$ contacts in the total number of intramolecular and intermolecular contacts, respectively. It can be seen that within the error calculation these values coincide (and are equal to the total fraction of parallel contacts in the system) although the fractions $\bar{m}_i/\bar{m}$ and $\bar{m}_e/\bar{m}$ of intra- and intermolecular contacts in the total number of contacts differ greatly.

At $\Delta\varepsilon = 0$ the fraction of parallel contacts in the system is small and virtually independent of concentration and when orientational effects exist, the fraction of parallel contacts increases with concentration.

The following conclusions may be drawn from *Figures 3–7*:

(1) Non-equivalence of contacts (orientational effects) has no significant effect on the state of chains in a dilute solution (in a good solvent).

(2) In concentrated solutions, orientational effects lead to chain extension accompanied by an increase in the mean length of their stiff segments. This increase can result in the appearance of the ordered liquid-crystalline state in polymers exhibiting high flexibility in the initial state in a dilute solution.

(3) Stiffening and extension effects become important only when a considerable difference in the energy of ordered (parallel) and disordered (defect) contacts of units or segments exists.

(4) In highly concentrated solutions the overwhelming majority of contacts are always of intermolecular type. The increase in the energetic advantage of parallel arrangement of units leads to an additional increase in the contribution of intermolecular contacts and, hence, to a decrease in chain folding.

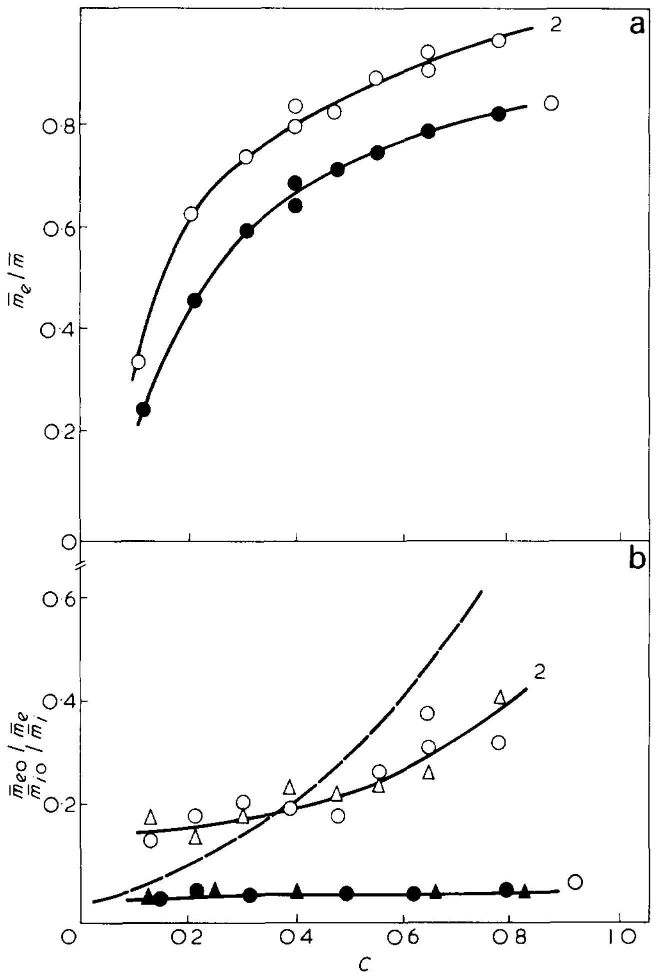


Figure 6 Concentration dependence of (a) fraction of intermolecular contacts $\bar{m}_e/\bar{m}$, and (b) fraction of favourable contacts among intramolecular $\bar{m}_{i0}/\bar{m}_i$ (△, ▲) and intermolecular contacts $\bar{m}_{e0}/\bar{m}_e$ (○, ●) for various values of the parameter $\Delta\epsilon$ (numbers at the curves). Dashed line gives the fraction of successful contacts calculated by equation (7) at $\Delta\epsilon = 2$ and $\epsilon_0 = 0$

DISCUSSION

The results of computer simulation show that orientational effects lead to chain stiffening with increasing polymer concentration. This is easily understood. Indeed, any chain bend can participate only in energetically unfavourable contacts. Since the number of contacts increases with polymer concentration, the energetic disadvantage of a bend also increases with it and, hence, the number of bends should decrease. An approximate analytical dependence can be found between the relative probability of a chain bend w_g/w_t (w_g is the probability of a *gauche* isomer and w_t is that of a *trans*-isomer) on the one hand and the polymer concentration and the magnitude of orientational effects on the other.

Let us consider two chain units (lattice points): unit 1 at the point of the chain bend and unit 2 in the middle of its stiff segment. Each unit can come into $z-2=4$ contacts with the neighbouring units ($z=6$ is the lattice coordination number). The probability of the appearance of each neighbour will be considered independent of energy and equal to C. When the contact is formed by unit 1, it is always included in the group of 'unfavourable' contacts and additional energy, $\Delta\varepsilon$, appears. Dividing this energy between the interacting partners we obtain the result that owing to contact the energy increased by $\Delta\varepsilon/2$.

For unit 2 both successful (with $\Delta\varepsilon=0$) and unfavourable contacts are possible. Neglecting the latter we obtain the approximate expression for the w_g/w_t ratio at a polymer concentration C:

$$\frac{w_g(C)}{w_t(C)} \simeq \frac{w_g(C=0)}{w_t(C=0)}\left[1-C+C\exp\left(-\frac{\Delta\varepsilon}{2}\right)\right]^{(z-2)} \tag{4}$$

Several other approximations are also used in equation (4). The contribution of intramolecular contacts and its change with concentration were neglected. The division of $\Delta\varepsilon$ between partners is not rigorous since various conformations of the second partner are possible. The assumption that the probability of the appearance of a neighbour is equal to C corresponds to the mean field approximation (see refs 1 and 2) which is not rigorous either[17]. Hence, equation (4) can be regarded as an approximation. In this approximation one can also obtain the concentration dependences of the unperturbed chain size:

$$\bar{h}^2 \simeq N[1-2w_g(C)]/2w_g(C) \tag{5}$$

the mean length of chain segments between bends:

$$\bar{\nu} = [4w_g(C)]^{-1} \tag{6}$$

and the average fraction of favourable contacts:

$$\frac{w_{\parallel}}{\bar{w}} \simeq w_t^2 = [1-4w_g(C)]^2 \tag{7}$$

The results are shown in *Figures 3, 4* and *6* by broken lines. It can be seen that they are in qualitative agreement with the computer simulation results.

Now the relationship between the initial Flory lattice model ($\Delta\varepsilon=0$) and the proposed model, taking into account orientational effects ($\Delta\varepsilon \neq 0$) on the one hand and real polymer systems on the other hand, will be considered.

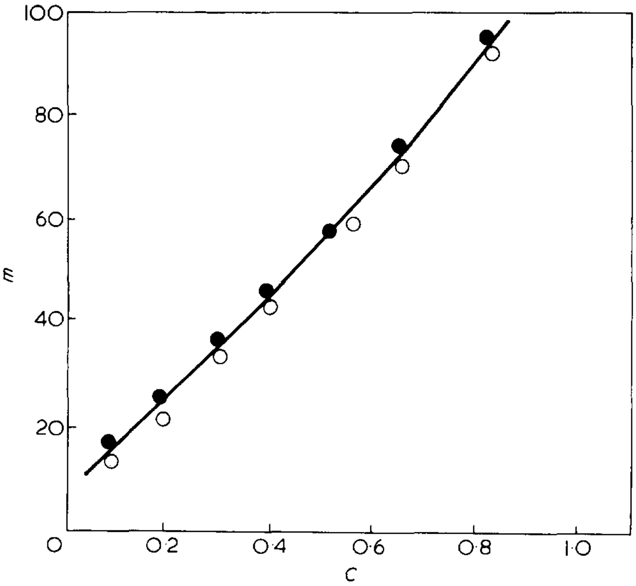


Figure 7 Total number of intra- and intermolecular contacts in the chain vs. concentration C; $\epsilon_0 = 0$, $\Delta\epsilon = 0$ (filled circles) and 2 (open circles)

A single chain unit in the lattice model occupies one cell of the lattice and is characterized by the equality of longitudinal and transverse dimensions. This unit represents a stiff part of the macromolecule, the length of which is close to the persistent length or the length of the Kuhn segment. For typical flexible polymer chains the main mechanism of distortion of short-range order is the rotational isomerism and therefore the chain becomes a system of rigid segments, the mean length and diameter of segments being similar. As to the character of segment interaction, the cases of stereochemically regular and irregular chains should be distinguished. Non-stereoregular atactic chains are characterized by chaotic arrangement of side groups which prevent dense packing of the segment approaching each other. Since regular arrangement is impossible, atactic flexible chains do not crystallize. Hence, these chains can be regarded as a complete defect and can be described by a simple lattice Flory model in which orientational effects are not taken into account. However, for stereoregular chains, parallel arrangement of contacting segments usually allows the dense packing similar to the crystalline packing. Any deviations from the parallel arrangement in most cases lead to the deterioration of packing and thus to the energetic disadvantage of these deviations. We assume, therefore, that the model in which orientational effects are taken into account is the correct one for the flexible stereoregular chains capable of crystallization. The spatial regularity of the lattice prevents the incorporation of the difference in packing density for parallel and 'defect' contacts. In the lattice model this difference is included in the parameter $\Delta\varepsilon$.

Another situation in which orientational effects may be significant is represented by a sample affected by the hydrostatic pressure. A bend or fold occupies a large volume and becomes more unfavourable than parallel chain parts under compression.

A considerable ordering and stiffening of macromolecules is observed only at $\Delta\varepsilon \gtrsim 1$ to 2. At present a realistic evaluation of $\Delta\varepsilon$ for specific polymers is not obtained. It could only be noted that this value should be very high for a lattice model in which the entire range of solvent strength from an athermic to an ideal solvent is $0 \leqslant -\varepsilon \leqslant 0.3$[29,30] (chain model on a cubic lattice is considered here). However, if $\Delta\varepsilon$ is taken to be 2, which corresponds to high orientational effects, one can conclude that the transition from a completely ordered (all chains are extended and arranged parallel to each other) to a completely random condensed state is accompanied by an increase in the energy of the unit (segment) by the value of $\Delta E = \Delta\varepsilon \cdot (z-2)/2$. At $T \simeq 300$K and $z = 6$ this gives $\Delta E \simeq 2.4$ kcal mol^{-1}. The experimental values of melting heat for common flexible-chain polymers are known to be ~10 kcal per segment[34] and about half this value is due to intramolecular effects (change in the number of *trans–gauche* isomers). From this standpoint the energy $\Delta\varepsilon$ of ordering of the model chains considered and the experimental values of melting heat for the flexible-chain polymers are comparable in order of magnitude. However, we do not know any experimental data indicating the dependence of the properties of the amorphous state of flexible-chain polymers on their stereoregularity. For polyethylene it has been shown by neutron scattering that the size of molecules in the melt coincides with that of unperturbed Gaussian coils under θ-conditions[8].

It is possible that orientational effects for such typical flexible-chain polymers as polyvinyl chains usually investigated are relatively low. One can expect, however, a high increase in these effects in chemically regular chains with strong intermolecular interactions, such as polyimide molecules[35]. They are known to exhibit high flexibility in dilute solutions. However, their properties in bulk, high mechanical strength and thermal stability are typical of stiff-chain polymers. These properties of polyimides are due to strong intermolecular interactions caused by the presence of cyclic groups in the main chain. The results obtained show that for polymers of this type one should expect chain stiffening in a concentrated solution and the appearance of the liquid-crystalline order due to orientational effects, i.e., to the non-equivalence of parallel and non-parallel contacts.

Our data indicate that possible local stereoregularity in stereoirregular chains can favour the appearance of elements of parallel arrangement and various supermolecular structures in amorphous polymers.

CONCLUSION

In the present work we only raised the problem of the influence of orientational effects on the structure of flexible-chain polymers rather than solved it, mainly because the calculations were carried out only for model chains at a single length $N = 61$. It was not investigated whether ordering appears as a result of phase transition or not; the scheme of computer simulation considered only the isotropic state of the system. Also, more dense filling of the space with polymer chains should also be considered. It would be reasonable to carry out a more detailed investigation within the framework of a lattice model by using the method of addition of subensembles[32] in the total volume (taking into account all possible types of ordered states of different sizes and shapes).

Naturally, the treatment of the structure of real polymers in the highly concentrated state is possible only when the methods of theoretical conformational analysis are used in which the specific stereochemical structure and geometry of molecules are taken into account. Owing to great difficulties in the calculations this approach can be used at present for the investigation of low molecular weight liquids only[36] and, hence, the study of simplified models for a polymeric amorphous substance is still an urgent problem.

The computer simulation carried out in this work made it possible to relate the properties of a model polymer system as a whole to a small number of parameters characterizing local interactions. It seems that the transition to the theoretical investigation of real concentrated polymer systems should be made (at least in the near future) by calculating the characteristics and parameters of the local interactions rather than by analysing the entire complex system as a whole. Subsequently these parameters should be used for calculations on the basis of simpler rough models, e.g. lattice models or models of a similar type.

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