Macromolecules 1984, 17, 415-418

Rotational Isomeric State Polymethylene Stars in Which Atoms Participating in Long-Range Interactions Behave As Hard Spheres

Wayne L. Mattice

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.
Received June 30, 1983

ABSTRACT: Expansion factors have been evaluated for tri- and tetrafunctional polymethylene stars and for selected fragments. A detailed rotational isomeric state model is used for unperturbed stars. Expansion is produced by forcing atoms participating in long-range interactions to behave as hard spheres. The longest chains in stars experience a greater expansion than do linear chains containing the same number of bonds. Examination of subchains shows that the extra expansion occurs primarily in that portion of the chain near the branch point. Subchains situated at chain ends experience nearly the same expansion in branched and linear molecules. While branching increases expansion of individual chains, overall expansion of the entire star is smaller than that of the linear chain of the same number of bonds, n. The reduced expansion of stars arises because the longest chain in a molecule of specified n contains fewer bonds as the functionality of the branch point increases. This latter effect is of greater consequence than the extra expansion of individual chains in the star.

Unperturbed branched macromolecules have smaller mean dimensions than linear chains containing the same number of bonds, n. The effect of branching on unperturbed dimensions is denoted by g_Θ, defined as $\langle s^2\rangle_{0,\mathrm{b}}/\langle s^2\rangle_{0,\mathrm{l}}$, where $\langle s^2\rangle$ denotes the mean square radius of gyration, zero as a subscript denotes the unperturbed state, and subscripts b and l denote, respectively, the branched and linear macromolecule.[1] Application of random flight statistics yields simple expressions for g_Θ for regular stars, molecules containing a single branch point from which emanate f branches containing n/f bonds.[1]

$$g_\Theta = (3f - 2)/f^2 \qquad (1)$$

Application of more detailed configurational statistics, such as that specified by rotational isomeric state[2-5] or wormlike chain[6] models, yields the same g_Θ for very large regular stars, but differences are seen in the nature of the approach to the limiting value.

Expansion of perturbed stars has been studied by several methods. Utilization of first-order perturbation theory,[7] studies of lattice chains,[8] and an approximate generator matrix model[9] predict a regular star experiences less expansion in a good solvent than does the linear chain containing the same number of bonds. Differing explanations have been offered for the smaller expansion of the stars. Emphasis is placed either on the fact that the number of bonds in the longest subchain in an f-functional regular star is proportional to $1/f$[7,9] or on a presumed expansion of the star at the Θ condition, thereby reducing possibilities for further expansion in a good solvent.[8,10]

Here we report expansion of perturbed tri- and tetrafunctional regular stars in which detailed attention is given to short-range interactions and chain geometry, including short-range interactions and geometry at the branch point. The corresponding linear chain is that specified by the customary rotational isomeric state model for linear polymethylene.[11] Rotational isomeric state models are also employed for tri- and tetrafunctional stars.[3,12] Perturbations are introduced by requiring chain atoms participating in long-range interaction to behave as hard spheres.[13,14] Points of interest are the comparative expansion of linear chains and regular stars, the extent of preferential expansion near the branch point, and an assessment of the error in simpler methods of estimating expansion of regular stars.

Calculational Methods

Samples of representative unperturbed linear chains were generated by using a priori and conditional probabilities and the chain geometry described by Abe et al.[11] for linear polymethylene. Perturbed linear chains were obtained by letting chain atoms participating in long-range interaction behave as hard spheres of diameter r^*.[13,14] Most of the results presented here were obtained by using $r^* = 2.7l$, where l denotes the bond length. Calculations were also performed by using smaller and larger r^*. Pairs of chain atoms were required to participate in long-range interactions if they were connected by eight or more bonds. A similar procedure was used for tri- and tetrafunctional stars. All first- and second-order interactions at the branch point were included in evaluation of a priori and conditional probabilities.[12] The statistical weights used were $\sigma = \tau = 0.43$ and $\omega = 0.0034$. Configuration-dependent properties were evaluated for two independently generated representative sets of molecules.

Results and Discussion

Unperturbed State. Figure 1 depicts characteristic ratios formulated from the mean square unperturbed radius of gyration of the linear chain, regular stars, and several fragments. The top of the figure is the asymptotic limit for linear chains. Horizontal arrows denote asymptotic limits for stars specified by the random flight expression for g_Θ.[1] Finite polymethylene stars have lower characteristic ratios, as expected.[2,6]

If n is small, short-range interactions at the branch point cause characteristic ratios of the main chains in the stars to be slightly smaller than those of the linear chain. The term "main chain" is used here to denote an arbitrarily selected chain of $n_{\mathrm{mc}} = 2n/f$ bonds in the f-functional star. A slight reduction in unperturbed dimensions is easily rationalized. The trans state is preferred by a bond in the middle of a long linear polymethylene chain because short-range interactions calling forth a statistical weight of σ are thereby avoided. First-order interactions for a bond to an atom which constitutes a trifunctional branch point contribute statistical weights of σ, σ, or σ^2, with a trans placement of the main chain being one circumstance producing a statistical weight of σ. Presence of a trifunctional branch point permits one of the gauche placements to compete on an equal basis with the trans placement. If the bond is to an atom which constitutes a tetrafunctional branch point, first-order interactions contribute statistical weights of σ^2 for all three rotational states. Both gauche placements now compete on an equal basis with the trans placement. First-order interactions

0024-9297/84/2217-0415$01.50/0

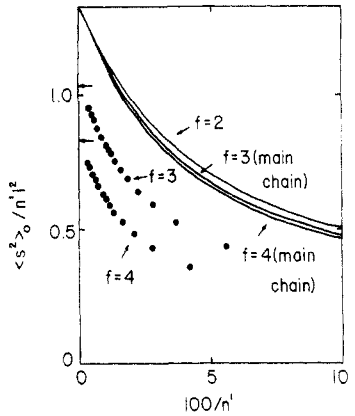

Figure 1. Characteristic ratios for unperturbed linear polymethylene chains or fragments (solid lines), trifunctional stars (●, $f = 3$), and tetrafunctional stars (●, $f = 4$). The number of bonds in the molecule or fragment is denoted by n'. Solid curves depict results for (upper curve) the linear chain or the external $^1/_3$ of the main chain in either star, (middle curve) the main chain (or internal $^1/_3$ of the main chain) for trifunctional stars, and (lower curve) the main chain (or internal $^1/_3$ of the main chain) for tetrafunctional stars.

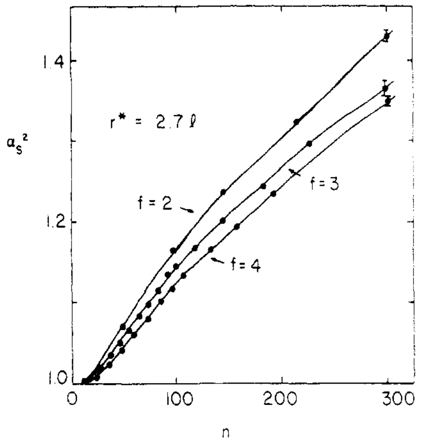

Figure 2. Expansion factors when r^* is 2.7 times the bond length. Bars for the largest molecules represent the range for two independent simulations. The branch point functionality is shown for each curve.

therefore decrease the probability that the main chain will have a fully extended configuration in the vicinity of a tri- or tetrafunctional branch point.[12] The influence of these short-range interactions is diluted as n_{mc} increases. Figure 1 shows that their effect on the characteristic ratios vanishes when n_{mc} reaches 10.[2]

Experimental determinations of g_Θ for large tri- and tetrafunctional stars are in good agreement with the prediction from eq 1.[15-17] Equation 1 underestimates g_Θ for stars of much higher functionalities, such as $f = 12$ or 18.[18]

Expansion Factors for Linear Chains and Stars. Figure 2 depicts expansion factors when r^* is 2.7 times the bond length. Branching produces a reduction in the expansion factor, $\alpha_s^2 = \langle s^2\rangle_{\mathrm{l}}/\langle s^2\rangle_{0,\mathrm{l}}$ or $\langle s^2\rangle_{\mathrm{b}}/\langle s^2\rangle_{0,\mathrm{b}}$. This conclusion is in harmony with those reached in several earlier studies.[7-10] One explanation advanced for the smaller α_s^2 in perturbed stars is based on an assumed expansion of branched molecules at the Θ condition.[8,10] There is then a reduced opportunity for further expansion when the branched molecule is transferred to a good solvent. However, rotational isomeric state stars considered in Figure 2 feel no perturbation whatsoever when $\langle s^2\rangle_{0,\mathrm{b}}$ is calculated because r^* is then zero. Their reduced expansion cannot be attributed to effects operative in the unperturbed state. Origin of the reduced expansion of tri- and tetrafunctional stars must be sought in the behavior of molecules perturbed with $r^* > 0$. The longest chains in a linear molecule or regular star contain $2n/f$ bonds. When molecules of the same n are compared, the longest chains become shorter with increasing f. Tri- and tetrafunctional stars experience the smaller expansion simply because they contain shorter chains.[7,9]

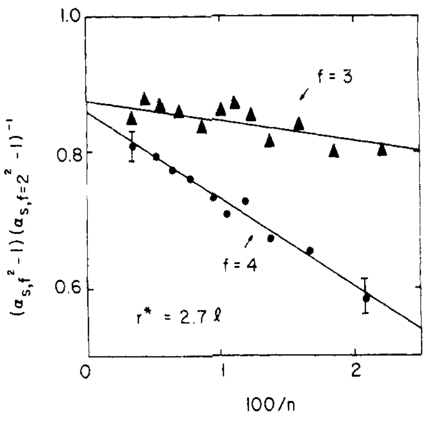

Figure 3. Extrapolation to infinite n of the relative expansion of regular stars and linear chains. Bars are shown for the largest and smallest tetrafunctional star.

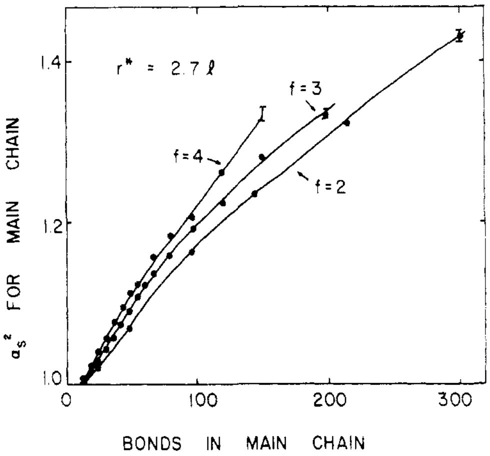

Figure 4. Expansion factors for main chains as a function of n_{mc}.

While qualitative conclusions expressed above are based on behavior of molecules containing 300 or fewer bonds, they can be used to estimate expansions for tri- and tetrafunctional stars of much larger n. In Figure 3 expansion factors are replotted as $(\alpha_{s,f}^2 - 1)/(\alpha_{s,f=2}^2 - 1)$ vs. $1/n$. Linear extrapolation to $1/n = 0$ is suggested. The resulting intercepts are definitely smaller than one. These intercepts can be treated as $\alpha_{s,f}^2/\alpha_{s,f=2}^2$ for very large tri- and tetrafunctional stars because $\alpha_{s,f}^2$ and $\alpha_{s,f=2}^2$ become much larger than one as n becomes infinite. The limiting value of g for the perturbed stars is then $g_\Theta(\alpha_{s,f}^2/\alpha_{s,f=2}^2)_{n\to\infty}$. Using eq 1 for evaluation of g_Θ, we estimate the limiting g to be about 0.68 and 0.54, respectively, for infinitely large perturbed tri- and tetrafunctional stars.

Expansion of the Main Chain. Mean square radii of gyration were computed for atoms in the main chains. Expansion factors for the main chains are depicted in Figure 4. Data presented for unbranched molecules are identical in Figures 2 and 4 because the linear chain is synonymous with the main chain. For the tri- and tetrafunctional stars, however, $n_{\mathrm{mc}} < n$ and $\alpha_{\mathrm{mc}}^2 < \alpha_s^2$. The former inequality is of greater consequence than the latter, causing α_{mc}^2 for stars to appear above those for linear chains in Figure 4. This order is the reverse of that seen with α_s^2 in Figure 2.

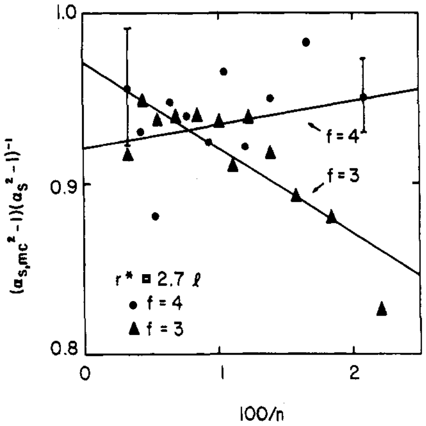

Figure 5. Extrapolation to infinite n of the relative expansion of main chains and stars.

The effect of the increased segment density in stars upon main-chain expansion is brought out in Figure 4. A linear chain of 150 bonds has α_s^2 near 1.24. If a chain of 75 bonds is attached to the 75th chain atom in this chain, the squared expansion factor for the chain of 150 bonds rises to about 1.28. Attachment of a second chain of 75 bonds to the same atom brings about a further increase to about 1.34. While the increased segment density in stars does indeed elevate expansion of the main chains, the effect does not dominate the behavior of α_s^2. A greater role is played by the decrease in n_{mc} with rising f at constant n.

Figure 5 compares expansion factors obtained for main chains and for all atoms in the stars. Contributions from the additional branches cause α_s^2 to exceed α_{mc}^2, but differences are rather small. Extrapolations to $1/n = 0$ suggest α_{mc}^2 differs from α_s^2 by less than 10% for very large perturbed tri- and tetrafunctional stars.

Preferential Expansion in the Interior of the Main Chain. Preferential expansion in the vicinity of the branch point is revealed by position dependence of the expansion of subchains. Two subchains, each containing $n_{mc}/3$ bonds, are selected for this purpose. The expansion factor for the subchain situated at an end of the main chain is denoted by α_{ext}^2. The other subchain is located in the middle of the main chain. Its expansion factor is denoted by α_{int}^2.

Figure 6 depicts α_{ext}^2 and α_{int}^2 for linear chains and for tri- and tetrafunctional stars. The behavior of α_{ext}^2 and α_{int}^2 differs in two important respects: In all cases $\alpha_{int}^2 > \alpha_{ext}^2$, and α_{int}^2 is much more sensitive to f than is α_{ext}^2. The relative insensitivity of α_{ext}^2 to f shows that the increase in α_{mc}^2 with f (Figure 4) arises from conformational effects that are localized in that portion of the main chain near the branch point.

It should be emphasized that preferential expansion in the middle of a main chain is not a feature unique to branched molecules. Figure 6 shows that linear chains also have $\alpha_{int}^2 > \alpha_{ext}^2$. Branching simply exaggerates effects that already exist in a linear chain. Preferential expansion in the middle of a linear chain has previously been documented for lattice[19] and rotational isomeric state[13,14] chains.

Approximation of α_s^2 for Regular Stars. A comparatively simple expression can be written for the expansion of regular stars based on the approximation that each chain behaves in the same manner as a linear chain containing the same number of bonds.[9]

$$\alpha_s^2 = \frac{(f-1)(1+2n/f)^2C_c - (f-2)(1+n/f)^2C_b}{(f-1)(1+2n/f)^2C_{0,c} - (f-2)(1+n/f)^2C_{0,b}} \qquad (2)$$

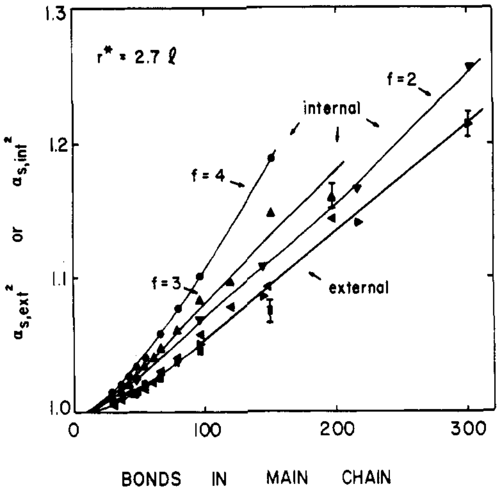

Figure 6. Expansion factors for subchains consisting of $^1/_3$ of the bonds in the main chain. The subchain is situated at the end of the main chain for α_{ext}^2 and in the middle of the main chain for α_{int}^2.

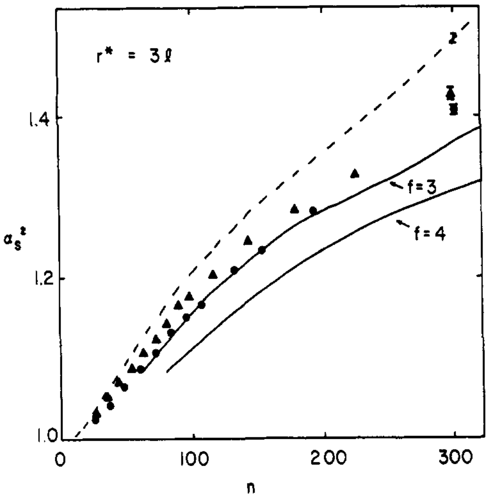

Figure 7. Comparison of expansion factors at $r^* = 3l$ for tri- and tetrafunctional stars, as estimated by eq 2 (solid lines) and as obtained by simulations (points).

Here C_c and C_b denote $\langle s^2\rangle/\sum l^2$ for linear chains of $2n/f$ bonds and n/f bonds, respectively. Equation 2 is expected to provide a lower bound for α_s^2 because it ignores the actual dependence of α_{mc}^2 and α_{int}^2 on f, as depicted in Figures 4 and 6. It also ignores the effect of the branch point on unperturbed dimensions (Figure 1), but this omission is important only at small n. The magnitude of the underestimate of α_s^2 is illustrated in Figure 7 for $r^* = 3l$. When n is 300, $\alpha_s^2 - 1$ is underestimated by about 15% for the trifunctional star and nearly 25% for the tetrafunctional star.

Equation 2 should provide an improved estimate if evaluation of C_c and C_b took account of the extra expansion of the main chains in the stars. Results depicted in Figure 6 demonstrate that adjustments should be made so that they affect the middle, but not the ends, of the main chains. Comparison of α_{mc}^2 and α_s^2 in Figure 5 suggests eq 2 might be accurate to within 10% if one utilizes correct results for C_c and C_b.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

References and Notes

(1) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(2) Mattice, W. L.; Carpenter, D. K. *Macromolecules* **1976**, *9*, 53.
(3) Mattice, W. L. *Macromolecules* **1977**, *10*, 511.

(4) Mattice, W. L. *Macromolecules* **1981**, *14*, 143.
(5) Mattice, W. L. *Macromolecules* **1982**, *15*, 1633.
(6) Mansfield, M. L.; Stockmayer, W. H. *Macromolecules* **1980**, *13*, 1713.
(7) Fixman, M. *J. Chem. Phys.* **1955**, *23*, 1656.
(8) Mazur, J.; McCrackin, F. *Macromolecules* **1977**, *10*, 326.
(9) Mattice, W. L. *Macromolecules* **1983**, *16*, 1623.
(10) McCrackin, F. L.; Mazur, J. *Macromolecules* **1981**, *14*, 1214.
(11) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
(12) Mattice, W. L. *Macromolecules* **1975**, *8*, 644.
(13) Mattice, W. L. *Macromolecules* **1981**, *14*, 1485.
(14) Mattice, W. L. *Macromolecules* **1981**, *14*, 1491.
(15) Roovers, J.; Bywater, S. *Macromolecules* **1972**, *5*, 384.
(16) Roovers, J.; Bywater, S. *Macromolecules* **1974**, *7*, 443.
(17) Hadjichristidis, N.; Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2521.
(18) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1983**, *16*, 214.
(19) Curro, J. G.; Schaefer, D. W. *Macromolecules* **1980**, *13*, 1199.

Temperature Dependence of the Hydrodynamic Radius of Flexible Coils in Solutions. 2. Transition from the Θ to the Collapsed State

Petar Vidaković[†] and Francis Rondelez*

Physique de la Matière Condensée,[‡] Collège de France, 75231 Paris Cédex 05, France.

Received March 18, 1983

ABSTRACT: The temperature and molecular weight dependence of the hydrodynamic radius R_H of flexible chains below the Θ temperature have been investigated by analytical ultracentrifugation. The measurements have been performed on high molecular weight polystyrenes ($M_w = 3.8 \times 10^6$, 4.48×10^6, 6.77×10^6, 8.42×10^6, and 20.6×10^6) of narrow polydispersity dissolved in two different solvents, cyclopentane and cyclohexane. All data can be represented on a single master curve if the expansion factor $\alpha_H = R_H(T)/R_H(\Theta)$ is plotted vs. the reduced variable $N/N_\tau = (\bar{M}_w|\tau|^2)/(n\alpha M_0)$. τ is the reduced temperature $|\tau| = |1 - \Theta/T|$ and $n\alpha M_0$ is an adjustable parameter $\simeq 150 \pm 30$ g mol^{-1}. The small N/N_τ values (<3) correspond to the so-called Θ domain in which the chain is essentially Gaussian and α_H is a constant close to unity. For large N/N_τ values (>20) the collapse domain is observed in which α_H varies as $\bar{M}_w^{-1/6}|\tau|^{-1/3}$. The molecular weight dependence of α_H demonstrates directly for the first time that the collapse domain is characterized by $R_H \sim \bar{M}_w^{1/3}$. The crossover between these two regimes is smooth and continuous. Our results are in agreement with the theoretical predictions advocating a continuous contraction for flexible chains in the temperature range between the Θ point and the coexistence curve. We have also observed a small residual molecular weight dependence in our scaled representation of α_H. This, the slight apparent dependence of $n\alpha M_0$ with the nature of the solvent and the difference between the $n\alpha M_0$ values above and below the Θ temperature, respectively, is yet to be explained.

Introduction

In the course of our general study on the temperature dependence of the hydrodynamic radius of flexible chains in solutions,[1,2] we have investigated the temperature range delimited by the Θ point on one side, and by the coexistence curve where phase separation will take place, on the other. As the temperature is lowered, the hydrodynamic radius R_H is expected to decrease sharply from its Θ value $R_H(\Theta) \sim N^{1/2}$ to its collapse value $R_H(T \ll \Theta) \sim N^{1/3}$ because of the increased attractive interaction between the monomer segments (N is the polymerization index). This latter relationship can be easily derived from the argument that in this asymptotic regime the internal globule concentration $c_i \simeq N/R_H^3$ is solely controlled by the steric repulsions between the individual segments and is no longer dependent on chain length. According to both classical mean-field theories and renormalization group approaches, R_H should vary as $N^{1/3}|\tau|^{-1/3}$ in the temperature domain where the chain contraction is taking place. On the other hand, the nature of the transition between the Gaussian and the collapsing behavior is still a matter of controversy between theoreticians. For sufficiently flexible and/or large chains, it is generally agreed that the transition should be smooth and continuous rather than discrete. A comprehensive review of the field has been recently published by Williams, Brochard and Frisch.[3] These authors also discuss the many experimental attempts to observe this coil–globule transition. In view of the vast arsenal of techniques put to use—small-angle neutron scattering,[4] viscosity,[5] and elastic and quasi-elastic light scattering[6-11]—the results have been rather disappointing. With one notable exception,[9,10] no group has reported evidence for a complete transition between the Θ state and the asymptotic collapse regime. Even in that case only the temperature variation of the chain radius has been investigated but not the molecular weight dependence, which would have given decisive proof that the chain was contracting to a globular state. It is true that the conditions necessary for the experiments are extremely stringent. Highly dilute solutions only must be used if single-chain contraction is to be observed rather than a spurious interchain penetration leading to aggregation and coalescence. An indirect advantage of dilution is that it widens the range of temperatures accessible between the Θ point and the demixion curve. Sharp molecular weight fractions are also a prerequisite to minimize fractional separation and avoid shifting the molecular weight distribution to smaller N as the temperature is lowered. Last, a meaningful comparison with theory requires extremely large molecular fractions ($N \simeq 10^5$). Unfortunately this requirement is somewhat contradictory with the other two.

[†] Permanent address: Odsek za Fizičke i Meteorološke Nauke Prirodno—Matematički fakultet, 11001 Beograd, P.O.B. 550, Yugoslavia.

[‡] Equipe de Recherche Associée au C.N.R.S. (E.R.A. 542).

0024-9297/84/2217-0418$01.50/0