pentenyl radical ($3T_A$) was found much larger than expected. In fact, this reaction has not been observed experimentally.[14] In the light of the HOMO level changes effected by TSI and TBI, we can now understand why the $3T_A$ structure gave this unusually high activation energy; inspection of Table 3 shows that this structure being N = odd framework has unfavorable TBI in addition to the probable HOMO elevating effect from the instability of product. We therefore conclude that the TS stability in small ω-alkenyl radical cyclization is not controlled by the decoupling effect (TSI) alone, but in greater degree it is determined by TBI and when n becomes larger (than 4) the product stability dominates the activation energy.

References

(1) P. Bischof, *Helv. Chim. Acta,* **63,** 1434 (1980). (b) M. J. S. Dewar and S. Olivella, *J. Amer. Chem. Soc.,* **101,** 4958 (1979).

(2) M. J. S. Dewar and S. Olivella, *J. Amer. Chem. Soc.,* **100,** 5290(1980).

(3) I. Lee, *Bull. Korean Chem. Soc., Tetrahedron;* in press.

(4) R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.,* **97,** 1285(1975).

(5) Transition state structures are designated as nT_A and nT_M for A and M routes, respectively, of radical cyclization of ω-alkenyl radicals with n methyl groups.

(6) M. J. Rothmann and L. Lohr, *Chem. Phys. Letter.* **70,** 405 (1980).

(7) N is different from n. When cyclization *via* A route, N equals n. On the contrary when, cyclization occurs *via* M route, N equals n+1.

(8) I. Fleming, "Frontier Orbitals and Organic Chemical Reaction", John Wiley, London 1976, p 19.

(9) SOMO stands for singly occupied whereas LUMO for lowest unoccupied MO's.

(10) (a) J. W. Verhovon, and R. S. Brown, *Tetrahedron,* **37,** 943(1981). (b) C. Sandorfy, R. Daudel and C. R. Hebd. *Seances Acad. Sci.* **93,**238(1954).

(11) R. Hoffmann, *Accounts Chem. Res.,* **4.** 1(1971).

(12) In Table, 3, odd and even systems are indicated as (o) and (e), respectively, with the transition state notation.

(13) (a) J. E. Baldwin, *J. C. S. Chem. Comm.,* 734 (1976); (b) J. E. Baldwin, J. Cutting, W. Dupont, L. Kruse, L. Silverman and R. C. Thomas, *ibid,* 736 (1976); (c) A. L. J. Beckwith and T. Lawrence, *J. C. S. Perkin 11* 1535 (1979); (d) A. L. J. Beckwith, C. J. Easton and A. K. Serelis, *J. C. S. Chem. Comm.* 482(1980.)

(14) P. Bischof, *Tetrahedron Lett.,* 1291(1979).

Molecular Dynamic Study of A Polymeric Solution (II). Solvent Effect

In Joon Oh, Young Seek Lee and Taikyue Ree[†]

Department of Chemistry, Korea Advanced Institute of Science and Technology, P. O. Box 150, Cheongyangni, Seoul 131, Korea (Received January 21, 1983)

Molecular dynamic method has been applied to a single polymer chain immersed in a solvent. The interactions for the pairs, of two solvent molecules (SS), of a chain element and a solvent molecules (CS), and of two non-neighbor chain elements (CC) are given by the Lennard-Jones potential, and the interaction between two bonded chain elements is given by a harmonic potential. We changed the CS interaction parameter ε_{CS} to 0.5, 1.0 and 2.0 times of the SS interaction ε_{SS}. We calculated the pair correlation functions for the SS, CS, and CC pairs, end-to-end distance and radius of gyration with the varying ε_{CS} parameters. The results showed that a phase separation occurs between the polymer and solvent in the 0.5 system where $\varepsilon_{CS}=0.5 \ \varepsilon_{SS}$. The autocorrelation functions for end-to-end distance and radius of gyration were also calculated.

1. Introduction

Polymeric systems are composed of very large numbers of small molecules, having very complicated intramolecular and intermolecular interactions. Especially, in the solution, these interactions are altered by solvents, and thus the conformation of the polymer chain is also altered by existence of the solvent molecules. The present theories in the literature do not take into account the details of the intramolecular

and intermolecular interactions due to the complication.[1,2]

It is possible to study such complicated systems by a computer simulation. There are three different methods available to study such systems, *i. e.,* molecular dynamics method[3-6], static Monte Carlo method[7-12] and "polymer reptation method"[13-17]. The advantage of a computer simulation is that the shape of the intra-and inter molecular potential functions can be controlled. Among the above three methods of simulation, the molecular dynamics method has some advantage,

i. e., both static and dynamic properties can be obtained by this method. We can also use this method for studying the solvent effects. There are however, only several works of polymeric systems simulated by this method.[3-6] In this work, we are interested to know how the interactions between the solvent molecules and the polymer chain affect the configuration and structure of the polymer chain. We assumed that the effect of the solvent is concerned only with the interactions between the solvent and the polymer chain, but not with the size of the solvent molecules. The details of the model used in this study will be discussed in the following section.

2. Polymer Solution Model

The model of a polymer chain in solution is the same as described in the previous paper.[6] A chain is represented by 20 monomer units linked linearly by springs obeying the harmonic oscillator–potential law

$$u(r_{i,i+1}) = \frac{1}{2}k_f(|r_{i+1} - r_i| - r_{eq})^2 \tag{1}$$

where k_f is the force constant of the spring, and r_{eq} is the equilibrium distance of the spring, *i. e.*, the bond distance. In the present work r_{eq} is chosen to be equal to the σ–parameter in the Lennard–Jones potential. The polymer chain is immersed in a solvent composed of N_s (=88) molecules in volume V. The interactions for a solvent-solvent molecule pair (SS), for a pair of a solvent molecule and a monomer unit of the polymer chain (SC) and for a pair of monomer units in the polymer chain (CC) were assumed to be the Lennard–Jones potential

$$u(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \text{ if } r \leq 2.62\,\sigma$$
$$= 0 \qquad\qquad\qquad \text{if } r > 2.62\sigma \tag{2}$$

we assumed that the σ–parameters for all the SS, SC and CC pairs are the same and are equal to that of methane, and the ε–parameters for the SS and CC pairs are assumed to be the same as that of methane. In order to investigate the solvent effect, we changed the ε–parameter for the SC pair to be equal to 0.5, 1 and 2 times of that of the SS pair. Hereafter, the systems with ε_{SC} equal to 0.5ε, ε and 2.0ε will be called the 0.5, 1.0 and 2.0 system, respectively. We used Verlet's explicit time–centered finite–difference algorithm[18,19] to integrate the equation of motion of the system. The details of molecular dynamics method are given elsewhere.[3-6,18,19] The calculations were performed at temperature, $T = 100°K$ and bulk number density $\rho = 0.75$, for the model polymer solution. The time step Δt was 10^{-14} sec, the force constant for the spring was assigned to be $k_f = 2 \times 10^5$ dyne/cm, and the equilibrium distance for the harmonic oscillator $r_{eq} = \sigma = 3.817\text{Å}$ as in Paper I.

3. Calculations and the Results

(1) *Pair Correlation Function g(r).* The pair correlation functions g(r) for the SS, CS and CC pairs were obtained by

TABLE 1: The Heights and Positions of the First Peaks of the Solven-tSolvent and Chain-Solvent Pair Correlation Functions

ε_{CS}	solvent–solvent		chain–solvent	
	height	position[a]	height	position[a]
0.5	2.47	1.12	0.89	1.12
1.0	2.31	1.12	1.63	1.12
2.0	2.26	1.12	3.00	1.12

[a] The length was given in σ units.

the following equation:

$$g(r) = \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r \rho} \tag{3}$$

where ρ is the number density of the system. The results obtained by our calculations for the three pairs are represented in Figure 1, 2 and 3, respectively, and the heights and the positions of the first peaks of the SS and CS g(r)'s are tabulated in Table 1. The SSg (r)'s (Figure 1) show that the height of the first peak changes with the interaction parameter ε_{CS}, *i. e.*, the height decrease if ε_{CS} increases. This is due to the reason that if ε_{CS} is large, many solvent molecules are attracted to the chain particles, as a result, the SS g(r) decreases, because we have fixed the number of solvent molecules, *i. e.*, $N_S = 88$. In other words, this is due to the finite sample size of the system, thus if we use a large number of solvent molecules, such a problem will not appear. However, the ε_{CS} effect does not
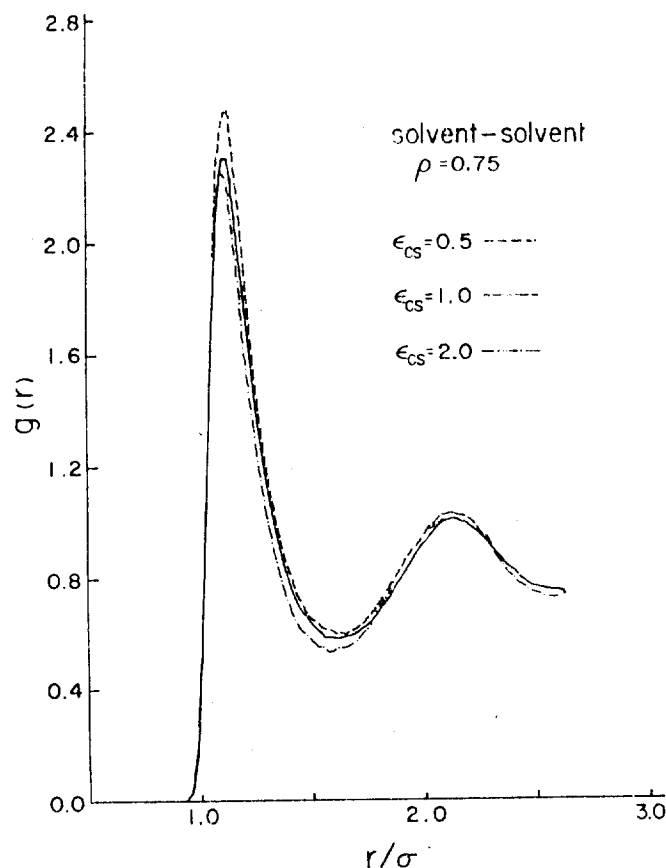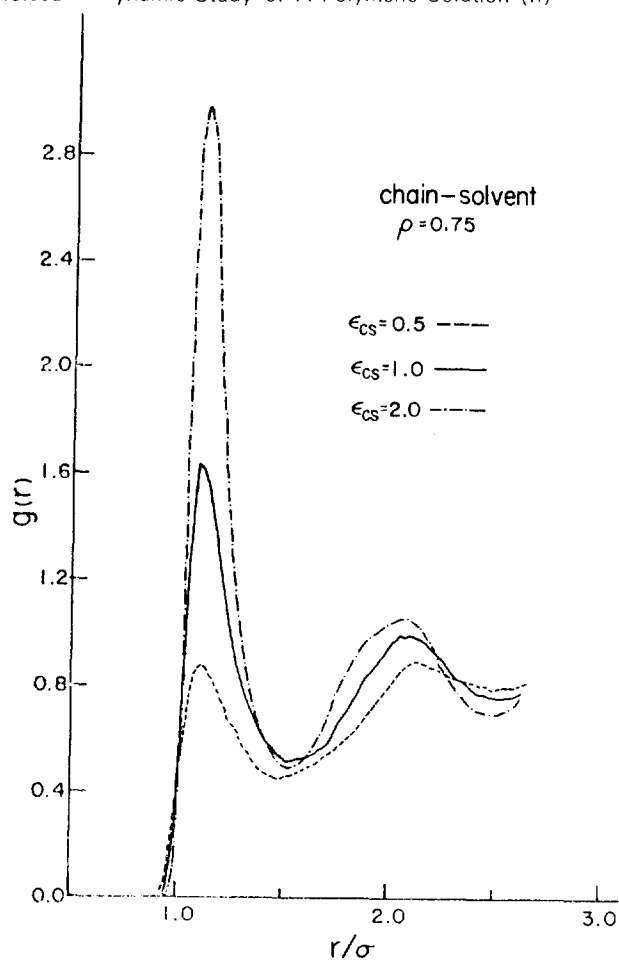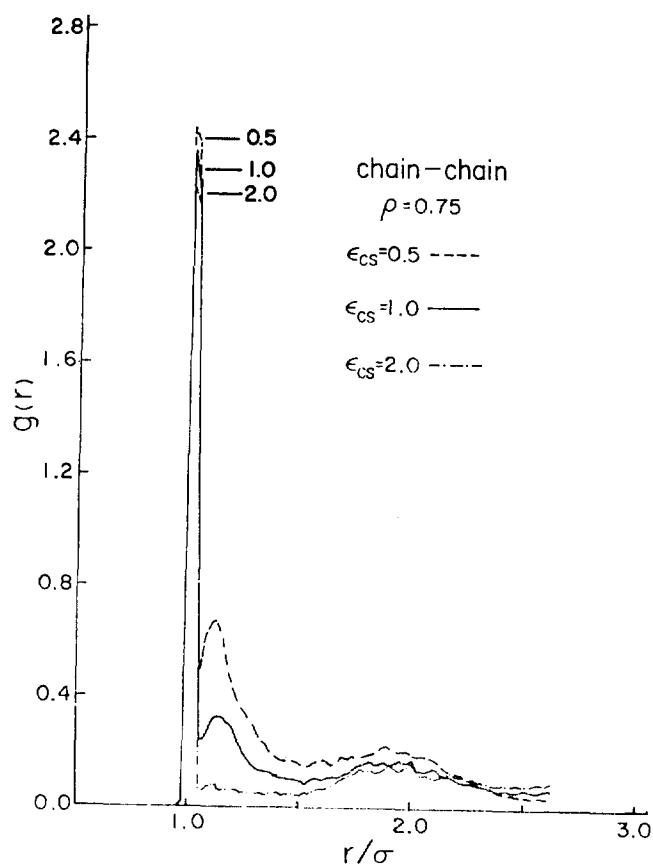

Figure 1. Pair correlation function g(r) between solvent–solvent molecules in the polymeric solution system, where the number density $\rho = 0.75$

Figure 2. Pair correlation function g(r) between a chain element and a solvent molecule in the polymeric solution system, where the number density $\rho=0.75$

Figure 3. Pair correlation function g(r) between the chain elements constructing the polymer in a solution system where the number density $\rho=0.75$

appear in the second layer (see Figure 1), *i. e.*, the SS g(r)'s for $\varepsilon_{CS}=0.5$ and $\varepsilon_{CS}=2.0$ superpose with the SS g(r) of $\varepsilon_{CS}=$ 1 which indicates the solvent system itself. From Figure 2 one can see that the height of the first peak of CS g(r) strongly depends on the CS interaction. In the 0.5 system, the height of the first peak is about half of that of the 1.0 system, *i. e.*, the probability for finding solvent elements close to a chain element is very samll in the 0.5 system. In the 2.0 system, the height of the first peak is about twice of that of the 1.0 system, *i. e.*, because of the strong interaction ε_{CS} ($=2.0\varepsilon$), solvent elements are highly concentrated near the reference chain element. From Figure 2, one also notes that a similar tendency appears in the second peak, *i. e.*, the height decreases as ε_{CS} decreases. Figure 3 shows the CC g(r). The first peak of the CC g(r) at $r/\sigma=1$ is due to the direct neighbors of a chain element, and also due to some other chain elements which will be close to distance σ, the bond length. The height of the first peak of the 0.5 system is slightly higher, and that of the 2.0 system is slightly lower than that of the 1.0 system. From this, one can easily know that more chain element can come close to the distance σ in the 0.5 system than in the 1.0 and 2.0 systems. This is due to the fact that the interaction between chain-solvent is the poorest in the 0.5 system, thus other chain elements can approach easily to distance σ close to the reference chain element around which a relatively small amount of

solvent molecules is found. On the other hand, in the 1.0 and 2.0 systems, because of stronger CS interactions, many solvent molecules are attracted to the reference chain element, and these attracted solvent molecules hinder other chain element to approach the reference chain element causing the decrease in CC g(r). The second peak at $r=1.12\sigma$ in Figure 3 is due to the same reason as in Paper I, *i. e.*, the 1.12 σ position is the L-J potential minimum point, thus other chain elements can approach to this distance from the reference chain element. In the second peak the height of the 0.5 system is considerable higher than that of 1.0 system, and no peak appears for the 2.0 system. The reason for the latter is due to the fact that all available positions of the L-J potential minimum are occupied by solvent molecules in the 2.0 system because of the strong CS interaction, thus other polymer element cannot approach this position. This conclusion is also supported by the first peak of the CS g(r) at $r=1.12\sigma$ in Figure 2 which shows a very large probability for finding solvent elements around the chain element in the 2.0 system than in the 0.5 and 1.0 system, *i. e.*, because of the large number of solvent molecules accumulated on the reference chain element, other chain elements cannot approach the latter. In Figure 3, the second peak of the 0.5 system is higher than that of the 1.0 system, this is due to the poor interaction in the 0.5 system (*i. e.*, $\varepsilon_{CS}=0.5\varepsilon$), a smaller amount of solvent molecules are attracted

to the reference chain element, thus, other chain elements can approach easily to the position of 1.12σ. Small and broad peaks are found at about 2.0σ of r in Figure 3, and these peaks are due to other chain elements in the second layer around a certain chain element. One also notes from Figure 3 that in the region of $r/\sigma > 2.35$, the CC g(r) of the 0.5 system decreases more rapidly than those of the 1.0 and 2.0 systems. This is due to the reason that in the 0.5 system, because of the poor interaction between chain-solvent, the chain elements can approach with each other more easily and closely than in the 1.0 or 2.0 systems, thus, the probability for finding chain elements over the region of $r \geqslant 2.35\sigma$ becomes very small. Consequently, one may consider that a system with poor interaction between chain and solvent will make a tightly aggregated shape in agreement with the facts which will be pointed out in the next section.

(2) *Configurational Properties.* The square of end-to-end distance R^2 (t) and the square of radius of gyration S^2 (t) of a chain molecule at time t are given by,

$$R^2(t) = [\mathbf{r}_1(t) - \mathbf{r}_{N_p}(t)]^2 \qquad (4)$$

and

$$S^2(t) = \frac{1}{N_p} \sum_{i=1}^{N_p} [\mathbf{r}_i(t) - \mathbf{r}_{cm}(t)]^2 \qquad (5)$$

where $\mathbf{r}_1$, $\mathbf{r}_{N_p}$ and $\mathbf{r}_i$ are the position vectors of the first, last and ith element constructing the polymer, respectively, and and the $\mathbf{r}_{cm}$ is the center-of-mass vector of the chain, and defined by

$$\mathbf{r}_{cm}(t) = \frac{1}{N_p} \sum_{i=1}^{N_p} \mathbf{r}_i(t) \qquad (6)$$

The averaged quantities, $\langle R^2 \rangle$ and $\langle S^2 \rangle$ values obtained by our simulations are summarized in Table 2. The $\langle R^2 \rangle$ and $\langle S^2 \rangle$ values for the 0.5 system are smaller compared with those values for the 1.0 system. The $\langle R^2 \rangle$ for the 2.0 system is smaller whereas $\langle S^2 \rangle$ is a little larger than the corresponding values of the 1.0 system. A component of the moment of inertia tensor at time t T_{ab} (t) is defined by the following equation:

$$T_{ab}(t) = \frac{1}{N_p} \sum_{i=1}^{N_p} [\mathbf{r}_i(t) - \mathbf{r}_{cm}(t)]_a [\mathbf{r}_i(t) - \mathbf{r}_{cm}(t)]_b \qquad (7)$$

where the subscripts a and b outside the brackets stand for x, y or z, and T_{ab} (t) is the ab component of the moment of inertia tensor at time t. The eigenvalues $\langle S_i^2 \rangle$'s (i=1, 2, 3) are tabulated in Table 2. They describe the shape of the chain molecule. In the 0.5 system, the three eigenvalues are almost equal, *i. e.*, the chain has almost a spherical shape. In the 2.0 system, the shape of the chain is a spheroid while that of the 1.0 system is an ellipsoid. (See Table 2). From the values of $\langle R^2 \rangle$, $\langle S^2 \rangle$ and the three eigenvalues of inertia tensor, one can easily understand that the chain has a tightly coiled shape in a poor solvent, *i. e.*, in the 0.5 system. The CS g(r) in the previous section showed that the probability for finding solvent molecules near a chain element is very low for the 0.5 system. These facts show that a

TABLE 2: **Chain configurational Properties: Mean Square End-to-End Distance** $\langle R^2 \rangle$, **Mean Square Radius of Gyration** $\langle S^2 \rangle$ **and Mean Eigenvalues of the Inertia Tensor**

| ε_{CS}	$\langle R^2 \rangle^a$	$\langle S^2 \rangle^a$	$\langle S_1^2 \rangle^b$	$\langle S_2^2 \rangle^b$	$\langle S_3^2 \rangle^b$
0.5	4.41	1.935	0.327	0.331	0.342
1.0	18.90	3.352	0.209	0.342	0.449
2.0	5.33	3.963	0.257	0.374	0.376

[a] The length was given in σ units; [b] $\langle S_i^2 \rangle$'s (i=1, 2, 3) were normalized by dividing by $\langle S^2 \rangle$.

phase separation occurs in a poor solvent where ε_{CS} is very small. In the 2.0 system, the solvent interacts most strongly with the chain. Thus, many solvent molecules are attracted (or adsorbed) to each polymer element. The solvent molecules attached to polymer elements interact with those attached to other polymer elements making the polymer chain in a lossely coiled spheroid form. (See $\langle S_i^2 \rangle$'s in Table 2) The 1.0 system has a large $\langle R^2 \rangle$, which is more than four times the $\langle R^2 \rangle$'s for the 0.5 and 2.0 systems, and it has a shape of prolated ellipsoid. The 1.0 system has $\varepsilon_{CS} = 1.0\varepsilon$ where ε is the interaction parameter for methane which equals ε_{SS} according to our model. Thus, for the 1.0 system, the relation $\varepsilon_{CS} = \varepsilon_{SS}$ holds. It seems that the latter relation holds generally for good solvents. And it is also well known that in good solvent, a chain molecule has an extended form. From this point of view, the large value of $\langle R^2 \rangle$ for the 1.0 system is a natural consequence since $\varepsilon_{CS} = \varepsilon_{SS}$ holds for the 1.0 system. On the other hand, the relation, $\varepsilon_{CS} \langle \langle \varepsilon_{SS}$, holds for poor solvents, and in the latter, a solute chain molecule will have a shape of tightly packed coil. Our 0.5 system may be considered as it belongs to this category since $\varepsilon_{CS} = 0.5\varepsilon_{SS}$. As already mentioned, in the 0.5 system, the chain molecule has a spherical shape. (See $\langle S_i^2 \rangle$'s in Table 2.) What will happen if a solvent is too good for a polymer molecule? For this case, the relation, $\varepsilon_{CS} \rangle \rangle \varepsilon_{SS}$, holds, and the 2.0 system may be regarded as belonging to this case since $\varepsilon_{CS} = 2.0\varepsilon$. We have pointed out in the above that the chain molecule in the 2.0 system has a spheroid shape (see the $\langle S_i^2 \rangle$'s in Table 2).

(3) *Chain Relaxation.* We calculated the time-dependent autocorrelation function $C\langle t; A \rangle$ by Eq. (8):

$$C(t; A) = \frac{\langle A(t_0) A(t_0+t) \rangle - \langle A(t_0) \rangle^2}{\langle A^2(t_0) \rangle - \langle A(t_0) \rangle^2} \qquad (8)$$

where A represents $R^2(t)$ or $S^2(t)$, the autocorrelation function means the extent to which a configuration at time t_0 influence of the configuration at time $t_0 + t$. The results obtained by our calculations are shown in Figures. 4 and 5. One can see from Figures 4 and 5 that the C(t; A)'s of the 0.5 system have larger values than those of the 1.0 system. This comes from the fact that the chain in a poor solvent is tightly aggregated and the interaction between chain and solvent is weak. Because of these reasons, the C(t;A)'s decay slowly than those of the 1.0 system. In the 2.0 system, the chain-solvent interaction is very large, thus in a small time region, the correlation function decreases more rapidly than the 1.0 system. But, over the large time region, because of
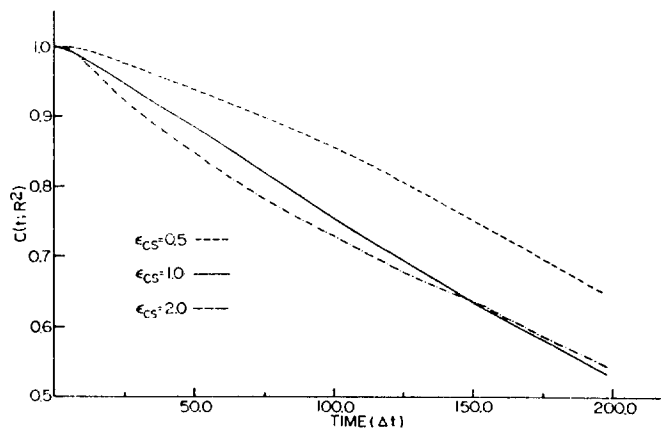
Figure 4. Autocorrelation function of the end–to–end distance. The time axis is shown in units of Δt
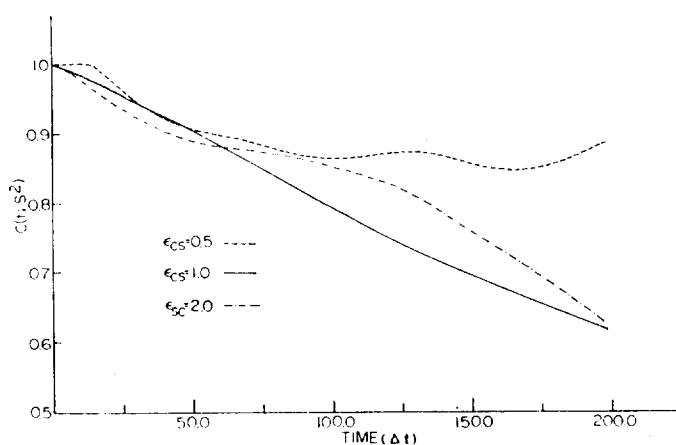
Figure 5. Autocorrelation function of the radius of gyration. The time axis is shown in units of Δt

the interaction between many solvent molecules attached to the polymer molecule, the latter makes a coil pretty tightly packed, thus the correlation function becomes larger than the 1.0 system, but smaller than the 0.5 system.

References

(1) H. Yamakawa, "Modern theory of the polymer solutions", Harper and Row publishers, New York, 1971.

(2) H. Morawetz, "Macromolecules in solution," John Wiley and Sons Inc., New York, 1965.

(3) D. C. Rapaport, *J. Phys.*, **A11**, L213 (1978); *J. Chem. Phys.*, **71**, 3299 (1979).

(4) M. Bishop, M. H. Kalos and H. L. Frisch, *J Chem. Phys.*, **70**, 1299 (1979).

(5) W. Bruns and R. Bansal, *J. Chem. Phys.*, **74**, 2064 (1981); *J. Chem. Phys.*, **75**, 5149 (1981).

(6) Y. S. Lee and T. Ree, *Bull. Korean Chem. Soc.*, **3**, 44 (1982).

(7) S. Windwer, "Markov Chains and Monte Carlo Calculations in Polymer Science" (Dekker, New York, 1970) and reference cited therein.

(8) F. T. Wall and J. Erpenbeck, *J. Chem. Phys.*, **30**, 634 (1959).

(9) Z. Alexandrowicz and Y. Accad, *J. Chem. Phys.*, **54**, 5338 (1971).

(10) R. Grishman, *J. Chem. Phys.*, **58**. 220 (1973).

(11) N. C. Smith and R. J. Fleming, *J. Phys.*, **A8**, 929 (1975).

(12) W. Bruns, *J. Phys.*, **A10**, 1963(1977).

(13) P. H. Verdier, *J. Chem. Phys.*, **59**, 6119(1973).

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

(14) P. H. Verdier, *J. Chem. Phys.*, **59**, 6119(1973).

(15) D. Ceperley, M. H. Kalos and J. L. Lebowitz, *Phys. Rev. Lett.*, **41**, 313 (1978).

(16) A. Baumgartner and K. Binder, *J. Chem. Phys.*, **71**, 2541 (1979).

(17) A. Baumgartner, *J. Chem. Phys.*, **72**, 871 (1980).

(18) L. Verlet, *Phys. Rev.*, **159**, 98 (1967).

(19) L. Verlet, *Phys. Rev.*, **165**. 201 (1968).