Chain dimension of a guest polymer in the semidilute solution of compatible and incompatible polymers

T. Nose

To cite this version:


HAL Id: jpa-00210232
https://hal.archives-ouvertes.fr/jpa-00210232
Submitted on 1 Jan 1986

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Chain dimension of a guest polymer in the semidilute solution of compatible and incompatible polymers

T. Nose

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

(Reçu le 15 mai 1985, accepté sous forme définitive le 12 novembre 1985)

Résumé. — Des chaînes polymériques (degré de polymérisation N) sont dissoutes dans une solution semi-diluée en bon solvant d’un autre polymère (degré de polymérisation P, concentration φ); on calcule le rayon de giration \( R_g \) et le second coefficient du viriel \( A_2 \) des chaînes \( N \) à partir des modèles de « blobs » thermiques et de concentration. Le paramètre renormalisé de volume exclu \( \psi \) a la forme \( \tau(\phi P^{\beta-1}, \chi) \) où \( \nu \) est l’indice du rayon en bon solvent \( (R_g \sim N^\nu) \) et \( \chi \) le paramètre d’interaction entre les deux types de polymères. On donne des expressions analytiques pour \( R_g \) et \( A_2 \), dont les lois d’échelles sont valables lorsque la concentration \( \phi \) dépasse la concentration de recouvrement \( \phi^* \):

\[
R_g \sim N^{\beta} f_2 \left( \phi N^{3\beta-1}, \tau(N^{1/(3\beta-1)})^{1/2} \right); \quad A_2 \sim N^{3\beta-2} f_2 \left( \phi N^{3\beta-1}, \tau(N^{1/(3\beta-1)})^{1/2} \right).
\]

Ces formes analytiques déterminent plusieurs régimes dont on discute les comportements caractéristiques. On trouve un collapse des chaînes \( N \) dissoutes dans des chaînes \( P \) beaucoup plus courtes \( (N \gg P) \) lorsque \( \phi = \phi^* \).

Abstract. — A small number of « guest » polymeric chains (index of polymerization \( N \)) are dissolved in a semidilute solution of a host polymer (index \( P \), concentration \( \phi \)) which is itself in a good solvent; the radius of gyration \( R_g \) and the second virial coefficient \( A_2 \) are studied on the basis of the thermal- and concentration-blob models. The renormalized excluded — volume parameter \( \psi \) has the form \( \tau(\phi P^{\beta-1}, \chi) \) where \( \nu \) is the index for the \( N \) — dependence of \( R_g \) in a good solvent \( (R_g \sim N^\nu) \) and \( \chi \) the interaction parameter between the guest and host polymers. Analytical expressions of \( R_g \) and \( A_2 \) are given as functions of \( N, P, \phi \) and \( \chi \), which have the following scaled forms for \( \phi > \phi^* \sim P^{1-\beta} \) (overlap concentration):

\[
R_g \sim N^{\beta} f_2 \left( \phi N^{3\beta-1}, \tau(N^{1/(3\beta-1)})^{1/2} \right); \quad A_2 \sim N^{3\beta-2} f_2 \left( \phi N^{3\beta-1}, \tau(N^{1/(3\beta-1)})^{1/2} \right).
\]

According to these scaled forms, several regions are defined, and the characteristic behaviour of each region is discussed. A concentration-dependent collapse of a \( N \)-chain in small \( P \)-chains \( (N \gg P) \) has been found around \( \phi = \phi^* \).

1. Introduction.

In the semidilute polymer solution, where polymer chains overlap strongly, a polymer chain behaves like a Gaussian chain even in a good solvent because of the screening effect. However, monomer distribution within a distance of correlation length is of an excluded-volume type where excluded-volume effects are not screened out [1, 2]. In this paper, an attempt will be made to extend this idea of excluded-volume effects on chain dimension to a more general case that a single chain of polymer A is dissolved in the semidilute solution of compatible or incompatible polymer B with a solvent being thermodynamically good for both polymer A and polymer B.

Radius of gyration of a linear polymer chain, \( R_g \), in a low molecular weight solvent, exhibits different dependences on the degree of polymerization \( N \) according to solvent goodness [1, 3, 4]:

\[
R_g \sim N^\nu
\]

with \( \nu \approx 3/5 \) in good solvent region \( (i) \), \( \nu \approx 1/2 \) in \( \Theta \)-region \( (ii) \), and \( \nu \approx 1/3 \) in globule region \( (iii) \) [5]. These regions are defined by the conditions \( N^{1/2} \tau > 1 \) (i), \( |N^{1/2} \tau| < 1 \) (ii), and \( N^{1/2} \tau < -1 \) (iii) [6], respectively, with \( \tau \) being the excluded-volume parameter. So, the boundary of these regions depends on \( N \) as well as solvent goodness \( \tau \). Similar situation may be expected for mean square distance between i-
and j-segments \( \langle r_{ij}^2 \rangle \) within a chain. That is, \( \langle r_{ij}^2 \rangle \) may follow
\[
\langle r_{ij}^2 \rangle \propto |i-j|^{2\nu}
\]
with \( \nu \) depending on \( \tau |i-j|^{1/2} \) in the same manner as \( \tau N^{1/2} \)-dependence of \( \nu \) in \( R_g \). Therefore, in a crossover region a chain does not expand uniformly, but, excluded volume effects depend on the size of partial chain we are looking at, and a single chain can be described as a succession of Gaussian blobs, each made of \( N \) segments, with excluded-volume interaction between the blobs [7]. Here, the parameter \( N \), defined by \( |\tau| N^{1/2} = 1 \), is a cutoff to separate Gaussian and excluded-volume regions. This treatment (called the thermal-blob model) was adopted by Weill and des Cloizeaux [8], and Ackasu and Han [9] for interpreting the crossover behaviour of \( R_g \) and hydrodynamic radius.

In the case of a chain in the semidilute solution, segment interactions beyond a certain distance (screening length \( \xi \)) are screened out by other polymers, and \( \langle r_{ij}^2 \rangle \) behaves like a Gaussian chain for \( \langle r_{ij}^2 \rangle^{1/2} > \xi \), i.e., \( r_{ij} \equiv \langle r_{ij}^2 \rangle^{1/2} \propto |i-j|^{1/2} \). Then, a labelled chain can be described as a succession of blobs, each having the size of \( \xi \), with no excluded-volume effect between the blobs (called the concentration-blob) [1]. Therefore, segment distribution of a labelled chain is controlled by \( \xi \) as well as \( N \). The above theoretical considerations are consistent with the temperature-concentration diagram presented by Daoud-Jannink [7] on the basis of scaling laws.

Applying the above arguments to the present ternary system, a guest polymer in the semidilute polymer solution with a good solvent, we can expect that when \( r_{ij} \) is less than the correlation length \( \xi \) of the matrix solution the \( r_{ij} \) exhibits good-solvent type behaviour, whereas, when \( r_{ij} > \xi \), the chain can be regarded as a chain in a low-molecular-weight solvent with solvent goodness \( \tau \), but \( \tau \) in this case is the excluded-volume parameter for interactions between the blobs with dimension \( \xi \), depending on the concentration and molecular weight of matrix polymer as well as compatibility of polymer A with polymer B. The case of a labelled chain in the semidilute solution should be a special case that \( \tau \) is substantially zero (\( N \gg N \)), so that the chain is Gaussian when the observational scale is larger than \( \xi \), in consistence with a usual screening effect. A main problem in the ternary system, therefore, is to evaluate the excluded-volume parameter \( \tau \) as a function of concentration \( \phi \), polymeric index P of matrix polymer and segment-interaction parameter \( \chi \) between polymer A and polymer B.

In this paper following the above arguments, we present a theory for the excluded-volume effects in a guest polymer, derive expressions and expected scaling laws for \( R_g \) and the second virial coefficient \( A_2 \), and examine the dependences of \( R_g \) and \( A_2 \) on \( N \), \( P \), \( \phi \) and \( \chi \).

Theoretical and experimental studies on \( R_g \) and \( A_2 \) for the ternary system have not been made extensively as yet [11-16]. Joanny et al. [11] have theoretically treated a ternary system with \( \chi = 0 \) and \( N \neq P \) (i.e., bimodal mixture of chemically-identical polymers in good solvent) on the basis of scaling concepts (or blob model) to give the radii of gyration as a function of \( N \), \( P \) and \( \phi \). Recently, Tanaka [12] has presented a theory for concentration-dependent collapse of a large polymer in a solution of incompatible small polymers, predicting a discrete shrinkage of the large-polymers chain at a certain concentration with increasing concentration of the small polymer. Experimental studies from the above viewpoints have just been started except for a chemically-identical chain, that is, studies on polyvinylmethyllether in polystyrene/iodine solvents by Cotts [15] and polystyrene in polymethylmethacrylate/benzene or toluene by Kuhn et al. [16]. Some comparisons of the present theory with these experiments and existing theories will be made.

2. Description of the model.

2.1 SYSTEM. — Consider a guest polymer (2) in a polymer solution consisting of polymer (1) and solvent (0). The guest polymer and the matrix polymer are linear ones made of \( N \) and \( P \) statistical segments with a length \( a \), respectively. The concentration of the matrix polymer is \( \phi \) in volume fraction, while the concentration of the guest polymer is always infinitely diluted. The solvent is good for both polymers, and compatibility of the guest polymer with the matrix polymer ranges from good to poor. Namely, the interaction parameters \( \chi_{ij} \) between segments of \( i \)- and \( j \)-components are taken as
\[
\chi_{01} = \chi_{02} = 0
\]
\[
\chi_{12} = \chi
\]
where \( \chi \) is a variable changing from negative to positive, and the subscripts 0, 1 and 2 denote the solvent, the matrix polymer, and the guest polymer, respectively.

2.2 EXCLUDED-VOLUME PARAMETER \( \tau \).— We define a quantity \( g \) as the segment number of a host-polymer chain within the correlation length \( \xi \) of the matrix polymer solution, i.e.,
\[
\xi = a g^\nu
\]
where \( \nu_1 \) is the index \( \nu \) in good solvent region (i). When the concentration \( \phi \) is less than the overlap concentration \( \phi^* \), we have
\[
g = P
\]
for \( \phi < \phi^* \). For \( \phi > \phi^* \), we have [2]
\[
g = P(\phi/\phi^*)^{-1-3\nu_1} = \phi^{1-3\nu_1} \]
(3')
since $\zeta = aP^{\nu_1}(\phi^*)^{\nu_1/(1-\nu_1)}$ with $\phi^* \equiv a^3 P(aP^{\nu_1})^{-1}$.

As mentioned in the introduction, a guest chain can be described as a succession of blobs, each having the dimension $\zeta$. Within the blob, monomer distribution is of a good-solvent type, and each blob is made of $g$ segments, because equation (1) also holds for a guest polymer. To evaluate the interaction between the blobs, we define the excluded-volume parameter $\tau$ and the parameter $N_\zeta$ for $|i-j| > g$, where $N_\zeta$ is a cutoff to separate Gaussian and excluded-volume regions for $|i-j| > g$. Denoting the renormalized excluded-volume for a unit consisting of $n$ segments as $V(n)$ with $n = |i-j|$, we put

$$\tau^{-1} \equiv (N_\zeta/g)^{1/2} \sim r^3(g)/V(g) \quad (4)$$

where $r^3(g)$ indicates the volume of a blob. According to the classical theory, the excluded-volume parameter $\tau$ for the present ternary system is given by

$$\tau \sim \left[1 - (1 + \chi/2) \phi \chi P \right]/\left(1 + \phi P\right) \quad (6)$$

for $\phi \ll 1$ as a function of $P$, $\phi$, and $\chi$ (see Appendix).

The classical theory, however, cannot take the effect of chain-connectivity into account correctly, so that some modification must be necessary. The renormalized excluded-volume parameter may be expressed as

$$\tau^{-1} \sim \left[\frac{1}{2} - (1 + \chi/2) \phi \chi P \right]/\left(1 + \phi P\right) \quad (7)$$

which is obtained by a transformation of $P \rightarrow P_b$, $\phi \rightarrow \phi_b$ and $\chi \rightarrow \chi_b$ in equation (6) [2, 11], where $P_b$ is the number of blobs in a $P$-chain, $\phi_b$ is the volume fraction of the blobs of $P$-chains, and $\chi_b$ is the interaction parameter between blobs of the guest and host polymers: $P_b = P/g$; $\phi_b = (\phi/P) P_b = \phi g^{3\nu_1 - 1}$; $\chi_b = (\chi \phi g^{3\nu_1 - 1}) = \chi$ (note that the factor $\phi g^{3\nu_1 - 1}$ is the probability for another segment to be in an adjacent site [2]). This transformation leads the following facts.

(1) Equation (7) has the scaled form:

$$\tau = \left\{ \frac{1}{2} - (1 + \chi/2) \phi \chi \right\} \left(1 + \phi P\right) \quad (8)$$

(2) When $\chi = 0$, the renormalized $\tau$ (Eq. (7)) is reduced to $\tau \sim 1/(1 + \phi_b P_b)$ and to $\tau \sim g/P$ for $\phi \phi^* \gg 1$, which is exactly the same as the result obtained by Joanny et al. [11].

(3) From equations (7) and (5), when $\chi = 0$, $N_\zeta$ changes from $4g$ to $4g(N/g)^2$ ($\gg N$) around $\phi = \phi^*$ with increasing $\phi$, which is consistent with the normal screening effect.

2.3 MEAN DISTANCE BETWEEN THE $i$-TH AND $j$-TH SEGMENTS.

Following the thermal-blob theory [7-9], we assume ($n = |i-j|$)

$$\langle r^2 \rangle^{1/2} \equiv r(n) = \begin{cases} an^{v_2} = aq^{v_2}(n/g)^{v_2} & n \leq g \\ aq^{v_2}(n/g)^{v_2} & g < n \leq N_\nu \\ aq^{v_2}(N_\nu/g)^{v_2} & n > N_\nu \end{cases} \quad (9)$$

Here $v_2$ is the index $v$ for a Gaussian chain, i.e., $v_2 = 1/2$, and $v_3$ is $v$ in the excluded-volume region, i.e., $v_3 \simeq 3/5$ for $\tau > 0$ and $v_3 = 1/3$ for $\tau < 0$.

When the two-body interaction is attractive ($\tau < 0$) and dominant ($N_\nu < N$), the chain collapses and takes the globule state, so that in this region counter interaction to the attractive two-body interaction, which may be the three-body interaction, should be taken into account, which assures the stability of the system. This may be also the case in the $\Theta$-region.
In the thermal-blob theory, however, the assumptions for \( r(n) \) made in equation (9), i.e., the crossover at \( n = N_t \) and the power-law for \( n > N_t \) allow us to treat the case of \( \tau < 0 \) with no explicit evaluation of the counter interaction, and the assumption of \( \nu_3 = 1/3 \) (reciprocal of spacial dimensionality) for \( \tau < 0 \) assures the stability of the system. These assumptions may be rationalized if the counter interaction is a mild function of \( \phi, P \) and the temperature \( T \). We have no proof for that at this stage, but we can show that the three-body interaction estimated by the mean field approximation is a repulsive one with very weak dependence on \( P, \phi, \) and \( T \) in a ternary system (see Appendix). So, here, we adopt the thermal-blob concept, the expression of equation (9), even for \( \tau < 0 \), supposing that the counter interaction with repulsive force is substantially independent of \( \phi, P, \) and \( T \).

2.4 Renormalized excluded-volume. — As a crude expression, we may assume the renormalized excluded-volume \( V(n) \) as

\[
V(n) \sim \begin{cases} 
  r^3(n) & n \leq g \\
  (n/g)^{1/2} \tau^3(n) & g < n \leq N_t \\
  (\tau/\tau_1)^2 r^3(n) & n > N_t 
\end{cases}
\]

(10)

The second equation was derived from the requirement that \( N_t \) should be independent of the choice of unit-size \( n \) for \( g < n < N_t \). That is, we have \( N_t/n \sim (r^3(n)/V(n))^{2/3} \) (similar to Eq. (4)), then \( V(n) \sim \pm (n/N_t)^{1/2} r^3(n) = (n/g)^{1/2} \tau^3(n) \). Equation (9) gives a discrete change in \( V(n) \) at \( n = g \), while a continuous cross-over at \( n = N_t \). In reality, a change in \( V(n) \) may be very sharp around \( n \approx g \) in general, but not discrete.

2.5 Radius of gyration. — The definition of \( R_g \) is given by

\[
R_g^2 = \frac{1}{2N^2} \sum_{i,j} \langle r_{ij}^2 \rangle = \frac{1}{N^2} \sum_{n=1}^{N} (N - n) [r(n)]^2
\]

(11)

From equations (11) and (9), we have

\[
R_g^2 = a^2 N^{2v_1}/2(2v_1 + 1)(v_1 + 1)
\]

for \( N \leq g \),

\[
R_g^2 = a^2 N^{2v_1} \left[ \frac{(g/N)^{2v_1 + 2}}{(2v_1 + 1)(2v_1 + 2)} + \frac{2(v_2 - v_1)(g/N)^{2v_1 + 1}}{(2v_1 + 1)(2v_1 + 2)} (1 - g/N) \right] + \frac{(g/N)^{2v_1 - v_2}}{(2v_2 + 1)(2v_2 + 2)} \left[ 1 - (g/N)^{2v_2 + 2} \right]
\]

(13)

for \( g < N \leq N_t \) and

\[
R_g^2 = a^2 N^{2v_1} \left[ \frac{(g/N)^{2v_1 + 2}}{(2v_1 + 1)(2v_1 + 2)} + \frac{2(v_2 - v_1)(g/N)^{2v_1 + 1}}{(2v_1 + 1)(2v_1 + 2)} (1 - g/N) \right] + \frac{(g/N)^{2v_1 - v_2}}{(2v_2 + 1)(2v_2 + 2)} \left[ 1 - (g/N)^{2v_2 + 2} \right]
\]

(14)

for \( N_t < N \). Here we have used the approximation

\[
\sum_{n=1}^{N} n^K \approx N^{K+1}(K+1)^{-1}
\]

(15)

because \( N \) is assumed to be large enough.

2.6 Second virial coefficient. — The second virial coefficient \( A_2 \) of osmotic pressure is given by (see Appendix)

\[
A_2 = N_A V(N)/2(NM_\phi)^2
\]

(16)

which can be calculated from equations (16) and (10) with \( n = N \) using the results in section 2.5, where \( M_\phi \) is the molecular weight of a segment of the guest polymer.

Now, equations for \( R_g \) and \( A_2 \) are given as functions of \( g \) and \( N_t \), which are evaluated by equations (2), (3), and (5) with equation (7). Then, \( R_g \) and \( A_2 \) can be calculated as a function of \( \phi, P, N, \) and \( \chi \).
3. Results and discussion.

3.1 SCALING LAW. — Expressions of \( R_g \) and \( A_2 \) obtained in the preceding sections have the following scaled forms:

\[
R_g(N; P, \phi, \chi) = a N^{\nu_1} f_R \left\{ gN, \tau(N/g)^{1/2} \right\}
\]

(17)

which is reduced to

\[
\phi/\phi* < 1
\]

\[
R_g = R_g0 f_R \left\{ PN^{-1}, \tau(NP^{-1})^{1/2} \right\}
\]

(18)

where \( R_{g0} = a N^{\nu_1} \), and

\[
A_2(N; P, \phi, \chi) = \frac{N_A(a N^{\nu_1})^3}{2(N M_0^2)^2} f_A(g/N, \tau(N/g)^{1/2})
\]

(20)

which is reduced to

\[
\phi/\phi* > 1
\]

\[
A_2 = A_20 f_A \left\{ PN^{-1}, \tau(NP^{-1})^{1/2} \right\}
\]

(21)

where \( A_{20} = N_A(a N^{\nu_1})^3/2(N M_0^2) \).

3.2 ASYMPTOTIC BEHAVIOURS. — According to the above scaled forms, we may define several regions for the semidilute solution (\( \phi/\phi* > 1 \)), each exhibiting characteristic behaviour of \( R_g \) and \( A_2 \). That is,

1. \( \phi N^{3\nu_1-1} < 1 \) \( (N < g) \)

(II-1)

2. \( \phi N^{3\nu_1-1} > 1 \) \( (N \geq g) \)

(II-2)

In region I, the presence of matrix polymers has only a very weak influence on the intra- and inter-molecular interactions of a guest-polymer chain so that the chain is essentially of good solvent type:

\[
R_g = R_g0 \phi_0 f_R(\phi N^{3\nu_1-1}, 0)
\]

\[
\sim a N^{\nu_1}(\phi N^{3\nu_1-1})^\chi
\]

(26)

\[
\sim a N^{\nu_2} \phi^{3\nu_1-1}
\]

(27)

which can be derived from the requirement that \( R_g \propto a N^{\nu_2} \) at a fixed \( \phi \). Then, equation (22) is reduced to

\[
A_2 \sim A_20 \tau(N^{3\nu_1-1})^{1/2} R_{g0}^2(a N^{\nu_1})^3
\]

\[
\sim A_20 \tau N^{\frac{1}{2} + \frac{3(\nu_1-\nu_2)}{1-\nu_1}} \phi^{\frac{1+6\nu_1-6\nu_2}{6\nu_1-2}}
\]

(28)

In region II-1, the excluded-volume effect is dominant, and we can put (note Eq. (27))

\[
R_g = a N^{\nu_2} \phi^{3\nu_1-1} f_R \left\{ \left| \tau \right| \left( N^{3\nu_1-1} \right)^{1/2} \right\}
\]

(29)

\[
\sim a N^{\nu_3} \phi^{3\nu_1-1} \left| \tau \right|^{3(\nu_1-\nu_2)}
\]

(30)

where the function \( f_R(\tau) \approx 1 \) at \( \left| \tau \right| \approx 1 \), and the second equation can be derived from the requirement of \( R_g \propto a N^{\nu_3} \) at fixed \( P \) and \( \left| \tau \right| \). Equation (29) is the scaled form for the whole range of region II. Then, \( A_2 \) is given from equation (22) as

\[
A_2 \sim A_20(\left| \tau \right|) R_{g0}^2(a N^{\nu_1})^3
\]

\[
\sim A_20(\left| \tau \right|) \left| \tau \right|^{6(\nu_1-\nu_2)} N^{3(\nu_1-\nu_1)} \phi^{3\nu_1-1}
\]

(31)

More explicit expressions for some special cases in region II will be shown in the following, where we put \( \nu_1 = \frac{3}{5}, \nu_2 = \frac{1}{2}, \) and \( \nu_3 = \frac{1}{3} \).

(1) Suppose the case that the polymer (1) and the polymer (2) consist of chemically identical monomers, i.e., \( \chi = 0 \). In this case, \( \tau \sim P^{-1} \phi^{-5/4} = \phi/\phi*^{-5/4} > 0 \) (from Eq. (7)). Then, for \( N < N^{5/4} < M_0^2 \phi/\phi*^{-5/4} < N^{1/5} / P \neq \phi/\phi*^{5/4} \) (Region II-1),

\[
R_g \sim a N^{1/2} \phi^{-1/8}
\]

(32)

\[
A_2 \sim A_20 N^{1/5} \phi^{1/4} / (\phi/\phi*)^{-5/4}
\]

(33)

\[
\sim (N_A a^3/M_0^2) P^{-1} \phi^{-1}
\]

(33')

and for \( N^{5/4} > M_0^2 \phi/\phi*^{-5/4} \), i.e., \( N/P > (\phi/\phi*)^{5/4} \) (Region II-2),

\[
R_g \sim a N^{3/5} (\phi/\phi*)^{-1/4}
\]

\[
\sim a N^{3/5} P^{-1/5} \phi^{-1/4}
\]

(34)

\[
A_2 \sim A_20 (\phi/\phi*)^{-3/4}
\]

(34')

\[
\sim (N_A a^3/M_0^2) N^{-1/5} P^{-3/5} \phi^{-3/4}
\]

(35)

(2) Near the \( \theta \)-point where \( \chi \) is non-zero but falls in a certain limited range, region II-1 is realized. That is, when \( \chi < \frac{1}{2} (\phi/\phi*)^{-5/4} \) or more precisely \( \left| \tau \right| = \left| \frac{1}{2} (\phi/\phi*)^{-5/4} - \chi \right| < (\phi/\phi*)^{-5/4} (N/P)^{-1} \right| 1/2 \leq 1 \),
one has

\[ R_g \sim a N^{1/2} \phi^{-1/8} \quad \text{with} \quad \phi = (2 \beta x)^{-4/5} \]  

(36)

\[ A_2 \sim A_{20} N^{1/5} \phi^{1/4} \left\{ \frac{1}{2} (\phi/\phi^*)^{-5/4} - \chi \right\} \]  

(37)

(3) Suppose the case that \( 1 > |\chi| > (\phi/\phi^*)^{-5/4} \nolimits \)
where \( \tau \sim -\chi(1 + \chi/2) \sim -\chi \). Then, we have the
following regions:

region II-1 : \( P^{-1} \phi^{-5/4} < |\chi| < (N^{-1} \phi^{-5/4})^{1/2} \)

(region II-1 requires the condition \( N/P < (\phi/\phi^*)^{5/4} \))

\[ R_g \sim a N^{1/2} \phi^{-1/8} \]  

(38)

\[ A_2 \sim A_{20} \chi N^{1/5} \phi^{1/4} \]  

(39)

region II-2 : \( |\chi| > (N^{-1} \phi^{-5/4})^{1/2} \) and \( |\chi| > (P^{-1} \phi^{-5/4}) \)

\[ R_g \sim a N^{3/5} |\chi|^{1/5} \]  

(40)

\[ A_2 \sim A_{20} |\chi|^{3/5} \chi < 0 \]  

(41)

\[ R_g \sim a N^{1/3} \phi^{-1/3} \chi^{-1/3} \chi > 0 \]  

(42)

\[ A_2 \sim -A_{20} |\chi|^{-1} N^{-4/5} \phi^{-1} \]  

(43)

3.3 Numerical results. — Putting the proportionality constant in equation (7) as 2 so that \( \tau = 1 \) when \( \phi < \phi^* \), and taking \( v_1 = 3/5, v_2 = 1/2 \) and \( v_3 = 1/3 \),
numerical values of \( \tau, R_g/R_g^0, \) and \( A_2/A_{20} \) were
calculated from the results in section 2.5 and 2.6, and
are represented in figures 1 ~ 5.

Figure 1 shows the excluded-volume parameter \( \tau \)
given by equation (7) against \( \log(\phi/\phi^*) \) for various
values of \( \chi \). With increasing \( \phi/\phi^* \), the value of \( \tau \)
decreases around \( \phi/\phi^* = 1 \) from unity to approach
a constant value which is characteristic for each value
of \( \chi \). The constant is given by \( \tau(\phi/\phi^* \rightarrow \text{large}) = -\chi(2 + \chi) \), that is, \( \tau = 0 \) for \( \chi = 0 \), \( \tau < 0 \) for \( \chi > 0 \),
and \( \tau > 0 \) for \( \chi < 0 \) in a realistic range of \( \chi \) where \( |\chi| \)
is not much greater than unity.

\[ \frac{R_g}{R_g^0} \]  

Fig. 2. — \( \log(\phi/\phi^*) \) and \( A_2/A_{20} \) as a function of \( \log(\phi/\phi^*) \)
for various values of \( N/P \) in case of \( \chi = 0 \). a : \( \log(\phi/\phi^*) \); \( \phi = 3/5, v_2 = 1/2, v_3 = 1/3 \).

b : \( A_2/A_{20} \) (The arrows \( \rightarrow \) in figure 2a indicate region II-2
for \( N/P = 10^4 \).

Figure 2 shows plots of \( \log(\phi/\phi^*) \) and \( A_2/A_{20} \)
against \( \log(\phi/\phi^*) \) as a function of \( N/P \) for a
chemically-identical polymer combination : \( \chi = 0 \).
In case of \( N/P < 1 \), as \( \phi/\phi^* \) increases, the chain
begins to shrink when \( \phi \) becomes comparable to \( N \),
and goes into an asymptotic region (\( \phi/\phi^* \gg 1 \) of
Gaussian type exhibiting \( R_g \propto \phi^{-1/8} \) (Eq. (32)).

On the other hand, in case of \( N/P > 1 \), \( R_g \) begins to
decrease around \( \phi/\phi^* = 1 \), and eventually reaches
the asymptotic region (II-2) of good-solvent type, where \( R_g \propto \phi^{-1/4} \)
holds (Eq. (34)), which is indicated by arrows for \( N/P = 10^4 \)
in figure 2. For each case, \( A_2 \) also shows a
characteristic behaviour. In case of \( N/P < 1 \), \( A_2 \)
sharply decreased at \( (\phi/\phi^*)^{5/4} = N/P \), while in case of
\( N/P > 1 \), \( A_2 \) gradually decreases around \( \phi/\phi^* = 1 \),
and reaches region II-1 (Eq. (33)), through region II-2
(Eq. (35)) when \( N/P \gg 1 \). In region II-2, \( A_2/A_{20} \) is
expressed by a universal function of \( \phi/\phi^* \) independent
of \( N/P \). In any cases, the value of \( A_2 \) tends to be zero
when the value of \( \phi/\phi^* \) increases.
Fig. 3. — log (Rg/Rgo) and A2/A2o as a function of log (φ/φ*) for various values of N/P in case of x = 0.1. a : log (Rg/Rgo); b : A2/A2o.

Figure 3 represents the φ/φ*-dependence of Rg/Rgo and A2/A2o for a case of incompatible polymer combination (x = 0.1 > 0) with various values of N/P. Similar to the case of x = 0, the chain dimension begins to decrease around φ/φ* = 1 for N/P > 1 and around g = N for N/P < 1 to eventually reach the asymptotic region (II-2) of Gaussian type with the power of −1/3 : Rg oc φ−1/3 (Eq. (42)). It is quite interesting that Rg decreases more dramatically around φ/φ* = 1 with increasing value of N/P, which will be discussed in detail later. Corresponding to the above behaviour of Rg, the A2-value changes from positive to negative at g = N for N/P < 1 and gradually decreases around φ/φ* = 1 for N/P > 1, then increases with the power of −1(A2 oc −φ−1), becoming very small in magnitude. It should be noted that the concentration at which A2 = 0 correspond to the concentration at which Rg begins to shrink. Therefore, even at A2 = 0, the chain dimension is still expanded and almost equal to that in a good solvent, which is due to the fact that repulsive excluded-volume effects still prevail between segment pairs within the chain at A2 = 0.

Figure 4 shows the results of Rg and A2 for a case of compatible polymer combination (x = −0.1 < 0) with various values of N/P. No essential change in Rg is found, i.e., the excluded volume is always positive, but the decrease in Rg appears around g = N for N/P < 1 and φ/φ* = 1 for N/P > 1 by a certain amount corresponding to the change in r-value from r(φ = 0) = 1 to r(φ/φ* ≳ 1) = |χ| (Eq. (40)). Similar to the other cases, the A2-value decreases sharply at g = N for N/P < 1, or gradually around φ/φ* = 1 for N/P > 1, but tends to take a positive constant-value (Eq. (41)) because of compatible combination. For the case of N/P < 10−1, one can see that the A2-value increases once after a sharp decrease, then decreases gradually, corresponding to region I (g < N < Nt) and II (N > Nt), respectively. The increase in A2-value in region I is due to a good compatibility of the two polymers.

Figure 5 represents the N/P-dependence of Rg and A2 at φ/φ* = 10 for various values of χ. (Here, note that Rg oc N3/5 and A2 oc N−1/5.) The N- and P-dependences of Rg/Rgo and A2/A2o are described.
Fig. 5. - log (Rg/Rg0) and A/A20 as a function of log (N/P) for various \( \chi \)-values at \( q_1/q_1^* = 10 \). a: log (Rg/Rg0); b: A2/A20.

As pointed out already, when \( \chi = 0 \) the excluded-volume parameter \( \tau \) has the same form as that of Joanney et al. [11], so that the present results for asymptotic behaviours of \( R_g \) of N-chain recover their results: \( R_g/R_{g0} = 1 \) for \( \phi/\phi^* < 1 \); \( R_g/R_{g0} \propto (\phi/\phi^*)^{-1/4} \) (Eq. (34)) for \( (N/P)^{1/5} > (\phi/\phi^*) > 1 \), and \( R_g/R_{g0} \propto \{ (\phi/\phi^*) (N/P)^{4/5} \}^{-1/8} \) (Eq. (32)) for \( (\phi/\phi^*) > (N/P)^{4/5} \) (see also table II in Ref. [11]).

As seen in figure 3, we found a sharp decrease in \( R_g \) of N-chain in small P-chain around \( \phi \approx \phi^* \) with increasing concentration \( \phi \) of P-chain. Tanaka [12] has theoretically predicted a similar transition from coil to globule at the limit of \( N/P \to \infty \). According to his theory, it is the first-order transition occurring at \( \phi \approx P^{-1} \), whereas, in the present theory, \( R_g \) changes drastically but continuously at \( \phi \sim \phi^* \sim P^{-4/5} \). The mean-field approximation in Tanaka’s theory may be responsible for the different \( P \)-dependence of transition concentration. In fact the excluded-volume parameter \( \tau \) of equation (6) by the mean-field theory changes from positive to negative at \( \phi \sim P^{-1} \) which is less than the overlap concentration \( \phi^* \sim P^{-4/5} \). The continuity of \( R_g \) at the transition in the present theory is due to the continuous change in \( \langle r_0^2 \rangle \) at \( n = N_1 \) (Eq. (9)).

As far as the thermal-blob model is used, the transition should be mild, having no singularity. So, the collapse found here is not a real transition but only a rapid shrinkage of the coil with increasing \( \phi \). Retaining the expression for \( \tau \), we can construct a theory for the case of \( \tau < 0 \) without using the thermal-blob model, for example, with using the Flory-type calculation of excluded-volume effects [5] or other approaches [6]. However, whether the collapse is of the first-order or a mild shrinkage is still an open question both theoretically and experimentally [17-19].

The results for \( R_g \) and \( A_2 \) in case of \( \chi = 0 \) with \( P = N \) have been basically verified by experiments with neutron scattering [2]. \( P \)-dependences of \( R_g \) and \( A_2 \) in chemically-identical chains have been measured by Kirste and Lehnen [20], but, for binary systems with no solvent so that direct comparison with the present results cannot be made. For a compatible polymer combination \( (\tau > 0) \), polystyrene (PS) in polyvinylmethyl ether (PVME)/toluene with \( N > P \), Cotts [15] has found that, with increasing concentration of PVME, \( A_2 \) decreases more rapidly in the range \( \phi > \phi^* \) than in \( \phi < \phi^* \), with \( A_2 \propto \phi^{-1} \) similar to the case of \( \chi = 0 \). Our theory does not conflict with this fact, suggesting a very small \( \chi \)-value for PS/PVME.

For an incompatible polymer combination \( (\tau > 0) \), polystyrene in polymethylmethacrylate (PMMA)/benzene (or toluene), Kuhn et al. [13], Rosen et al. [14] and Numasawa et al. [16] have found that \( A_2 \) vanishes at a certain concentration of PMMA which may correspond to \( \phi^* \). (Kuhn et al. showed that the concentration \( \phi_0 \) at which \( A_2 = 0 \) was proportional to the reciprocal of intrinsic viscosity [\( \eta \)]. Note [\( \eta \) \( \propto \)])

3.4 COMPARISON WITH EXISTING THEORIES AND EXPERIMENTS. — The present treatment is essentially based on the idea of Daoud et al. [2] for a labelled polymer chain in semidilute solution in good solvent. Therefore, when \( \chi = 0 \) and \( P = N \), our theory is reduced to the theory of Daoud et al., giving exactly the same results for \( R_g \) and \( A_2 \) at the semidilute limit: \( R_g \propto N^{-1/2} \phi^{-1/8} \); \( A_2 \propto N^{-1} \phi^{-1} \) (Eqs. (32) and (33)).
Rosen et al. and Numasawa et al. pointed out that even at \( A_2 = 0 \) (\( \phi = \phi_0 \)), the chain dimension of PS is almost the same as or slightly less than that in pure benzene, being much larger than the unperturbed dimension. This fact is quite consistent with the present result (Fig. 3). On the other hand, Kuhn et al. and Rosen et al. have found that the concentration \( \phi_0 \) was independent of temperature and molecular weight \( N \) and also that \( A_2 \) was represented by a single master curve of a function of \( \phi/\phi_0 \) for a fixed \( N \) with various \( P \) over the wide range of \( N/P \). Their findings seem to be in conflict with our theory (see Fig. 3) which predicts that, in a certain range of \( N/P < 1 \), \( \phi_0 \) should have \( N \)-dependence and \( A_2 \) is not a universal function of \( \phi/\phi_0 \). However, it is supposed that the \( N/P \) range and/or \( N \) range they used was not appropriate for detecting such theoretical predictions. In fact, Numasawa et al. have found for \( P > N \) that the temperature at which \( A_2 = 0 \) increases with increasing \( N \) and appears to level off at higher molecular weights (\( N \)), in consistence with the theory.

It should be noted that the present theory is too crude for quantitative descriptions of \( A_2 \) in real polymeric systems, because of a very crude approximation (Eq. (10)) with a discrete \( n \)-dependence of \( V(n) \).

Concentration-dependent collapse of \( N \)-chain in a small \( P \)-chain has not been found experimentally for synthetic flexible polymers in organic solvents, but DNA in polyethylene oxide/water [21]. Experiments are really interesting and needed to verify the occurrence of collapse and examine the \( P \)-dependence of the transition concentration.

### 4. Conclusions.

A theory for \( R_g \) and \( A_2 \) in a ternary semidilute solution has been presented by combining and extending the ideas of thermal- and concentration-blobs. The following results have been obtained:

1. An expression of the renormalized excluded-volume parameter \( \tau \) has been presented as a function of \( P, \phi \), and \( \chi \) (Eq. (7)).
2. Chain dimension \( R_g \) and \( A_2 \) are given in analytical forms as functions of \( N, P, \phi \), and \( \chi \).
3. These expressions of \( R_g \) and \( A_2 \) have the scaled forms represented by equations (17) ~ (22). According to these scaled forms, several regions are defined for \( \phi > \phi^* \), each exhibiting its characteristic behaviours of \( R_g \) and \( A_2 \) (Eqs. (24) ~ (31)).
4. A concentration-dependent collapse, which is not discrete but very sharp, has been predicted for \( N \gg P \) around \( \phi = \phi^* \).

### Appendix

**Calculation of Osmotic Pressure for a Ternary System.** Taking the solvent (0) and the matrix polymer (1) as diffusible components, and the guest polymer (2) as a non-diffusible component, we have the following equilibrium conditions:

\[
\mu_k(\delta \pi, \delta \phi_k) = \mu_k(0, 0) \quad (k = 0, 1)
\]

where \( \mu_k(\delta \pi, \delta \phi_k) \) is the chemical potential of \( k \)-component per mole when the pressure and the \( i \)-component volume-fraction \( \phi_i \) deviate from their mean values by the small amounts \( \delta \pi \) and \( \delta \phi_i \). From equation (A.1), we have

\[
\mu_k(\delta \pi, \delta \phi_k) = \mu_k(0, 0) + (\delta \mu_k/\delta P)_{T, \phi} \delta \pi + \sum_i (\delta \mu_k/\delta \phi_i)_{T, P, \phi_i \neq k} \delta \phi_i
\]

that is,

\[
\nu_k(\delta \pi/\partial \phi_2) + \sum_i (\partial \mu_k/\partial \phi_i)_{T, P, \phi_i \neq k} (\partial \phi_i/\partial \phi_2) = 0 \quad (k = 0, 1)
\]

where \( T \) is the absolute temperature, \( P \) the pressure, and \( \nu_k = (\partial \mu_k/\partial P)_{T, \phi} \) the partial molar volume of \( k \)-component. On the other hand, from the condition \( \sum \phi_i = 1 \), we have

\[
\sum_i (\partial \phi_i/\partial \phi_2) = 0.
\]

If we have expressions for \( \mu_k \) (\( k = 0, 1 \)) as a function of \( \phi_i \) (\( i = 0, 1, 2 \)), we can compute \( \delta \pi/\partial \phi_2 \) from equations (A.2) and (A.3). Here we adopt the Flory-Huggins theory, which gives the following expressions for the present case where \( P_0 = 1, \chi_{01} = \chi_{02} = 0 \), and \( \chi_{12} = \chi \) [22]:

\[
\frac{\Delta \mu_0}{RT} = \ln \phi_0 + (1 - 1/P_1) \phi_1 + (1 - 1/P_2) \phi_2 - \chi \phi_1 \phi_2
\]

\[
\frac{\Delta \mu_1}{RT} = \ln \phi_1 + (1 - P_1) \phi_0 + (1 - P_1/P_2) \phi_2 + P_1(1 - \phi_1) \phi_2 \chi
\]
where $\Delta \mu_i$ is the chemical potential of $i$-component per mole, the chemical potential of the pure liquid being taken as a standard, $R$ the gas constant and $P_i$ is the number of segments in an $i$-component chain.

From equations (A.2) and (A.3) with eqs. (A.4) and (A.5), we obtain

$$\frac{V_0}{RT} \frac{\partial \pi}{\partial \phi_2} = \frac{1}{P_2} + \frac{\phi_2}{\phi_1 + \phi_0/P_1} \left( \frac{1}{P_1} - (2 + \phi_0 \chi) \chi \phi_1 \right).$$  \hspace{1cm} (A.6)

Here, we have assumed $V_0 = \frac{V_1}{P_1}$. Expanding equation (A.6) in respect of $\phi_2$ at $\phi_2 = 0$, we eventually have

$$\frac{V_0}{RT} \frac{\partial \pi}{\partial \phi_2} = \frac{1}{P_2} + \frac{\phi_2}{\phi_{10} + \phi_0/\phi_1} \left( \frac{1}{P_1} - (2 + \phi_{00} \chi) \chi \phi_{10} \right) + O(\phi_2^2)$$  \hspace{1cm} (A.7)

where $\phi_{00}$ is $\phi_1 (\phi_2 \to 0)$ and $\phi_{10} + \phi_{00} = 1$. (Therefore, $\phi_{10}$ is $\phi$ in the test.) Since $(1/RT) (\partial \pi/\partial C') = (1/M_2) + 2 A_2 C' + \cdots$ and $C' = M_{20} \phi_2/V_0$, then the second virial coefficient $A_2$ is given by

$$A_2 = \frac{V_0}{M_{20}} \left( \frac{1}{2 P_1} - (1 + \phi_{00} \chi/2) \chi \phi_{10} \right) / (\phi_{10} + \phi_{00}/P_1).$$  \hspace{1cm} (A.8)

Here, $M_2$ is the molecular weight of the guest polymer and $M_{20}$ is the molecular weight of its segment, being equivalent to $M_0$ in equation (16).

To know a nature of the three-body interaction for a case of $\chi > 0$ that will give a negative $\tau$ at $\phi > \phi^*$, the third virial term of $\pi$ is calculated by taking the second derivative of equation (A.6) in respect of $\phi_2$ at $\phi_2 = 0$ under the condition of $\phi_{00}/\phi_1 = \text{constant}$ (constant composition of the matrix solution), for simplicity. That is, we have from equation (A.6)

$$\omega = \frac{1}{2} \left[ \frac{\partial^2}{\partial \phi_2^2} \left( \frac{V_0}{RT} \frac{\partial \pi}{\partial \phi_2} \right) \right] \phi_0/\phi_1 = \text{const} \mid \phi_2 = 0$$

$$= \frac{1 + \phi_0 \phi_1 P_1 \chi^2}{\phi_0 + P_1 \phi_1}$$

$$= \frac{1 + \phi_1 P_1 \chi^2}{1 + P_1 \phi_1} \quad \text{for} \quad \phi_1 \ll 1.$$  \hspace{1cm} (A.9)

The $\omega$-value is positive (repulsive interaction) and changes with $P_1 \phi_1$ as follows when $\chi > 0$, which may give the nature of the three-body interaction:

$$\omega \sim 1 \quad \phi_1 P_1 \ll 1 \quad \text{(dilute)}$$

$$\sim \chi \quad \phi_1 P_1 \sim 1/\chi \quad \text{(around} \ A_2 = \tau = 0)$$

$$\sim \chi^2 \quad \phi_1 P_1 \gg 1/\chi.$$  

The $\omega$-value exhibits a very mild change with $\phi_1 P_1$ and $T$, having no singularity at $A_2 = 0$. (Note that $\chi$ may change gradually with $T$.)

References

[6] This criterion for the region (iii) has not been established yet even other than the logarithmic-term correction [5]. See for instance Allegre, G., Gianazzoli, F., *Macromolecules* 16 (1983) 1311. It should also be noted that three-body interactions must be taken into account for describing a detailed nature of the collapse and interpreting the $\Theta$- and the globule regions more correctly [5]. Joanny and Brochard, *J. Physique* 42 (1981) 1145, have theoretically predicted a strong contraction of a polymer chain in a melt of incompatible polymer chains similar to the usual collapse of a single chain in a poor solvent.