Effects of Chain Ends on the Third Virial Coefficient for Polymer Chains. Oligo- and Polystyrenes and Oligo- and Poly(methyl methacrylate)s

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ABSTRACT: In light of the recent analysis of the second virial coefficient A_2 for flexible polymers, the third virial coefficient A_3 is reformulated for the helical wormlike chain, taking account of possible effects of chain ends. It is shown that at the Θ temperature at which the effective binary-cluster integral vanishes, and hence A_2 vanishes for large molecular weight M, the nonvanishing part $A_{3,\Theta}$ of A_3, which results from various kinds of ternary-cluster integrals, becomes appreciably dependent on M as M is decreased. It is then shown that the theory may explain satisfactorily the data obtained for $A_{3,\Theta}$ in the preceding paper for atactic oligo- and poly(methyl methacrylate)s in acetonitrile at 44.0 °C (Θ) and in the previous and present studies for atactic oligo- and polystyrenes in cyclohexane at 34.5 °C (Θ). The values obtained for effective excess ternary-cluster integrals associated with the chain end beads are of the reasonable order of magnitude.

Introduction

Recently we have started a reinvestigation of the excluded-volume effects in dilute polymer solutions.[1,2] In particular, it has then been shown theoretically and experimentally that there remain appreciable effects of chain stiffness and chain ends on the second virial coefficient A_2 even for rather large molecular weight M,[1,3–5] indicating that the two-parameter theory[6] of A_2 breaks down. On the other hand, in the past several years there has been some renewal of activity in theoretical and experimental studies of the third virial coefficient A_3.[7–11] In these, one of the important conclusions[8] is that, because of three-segment (ternary-cluster) integrals β_3, A_3 never vanishes at the Θ temperature as defined as the (M-independent) temperature at which A_2 vanishes for large M. This also indicates the breakdown of the two-parameter theory. In light of the recent reinvestigations of A_2 above, it is then important to also study possible effects of chain stiffness and chain ends on A_3. The former effect has recently been, to some extent, considered by Norisuye et al.[10] Thus the object of the present paper is to examine the effect of chain ends on A_3, especially at the Θ temperature.

Historically, the foremost of earlier experimental studies of A_3 is that by Flory and Daoust,[12] who carried out osmotic pressure measurements for polyisobutylene (PIB) in benzene and concluded that A_3 was negligibly small at Θ. A similar conclusion was later arrived at by Krigbaum and Geymer,[13] who also made osmotic pressure measurements for atactic polystyrene (a-PS) in cyclohexane. Subsequently, however, it was found for several polymers, including PIB and a-PS, that this was not necessarily the case.[14–17] Very recently, Norisuye and co-workers[7–11] have made an extensive light-scattering study of A_3 in Θ and good solvents and concluded that, for a-PS in cyclohexane at Θ,[8] it is definitely positive and almost independent of the weight-average molecular weight M_w for $M_w \gtrsim 2.0 \times 10^4$.

In the present paper, we first evaluate theoretically the effect of chain ends on A_3 along a line similar to the previous analysis of the same effect on A_2.[1] By the use of this theory, we then analyze the data for A_3 obtained in the preceding paper[5] for atactic oligo- and poly(methyl methacrylate)s (a-PMMA) in acetonitrile at Θ and also those obtained in the previous[4] and present studies for a-PS samples, including the oligomers, in cyclohexane at Θ, together with those of Norisuye et al.[8] (Recall that the a-PS samples have an n-butyl group at one end of the chain and a hydrogen atom at the other.)

Theoretical Section

In general, A_3 may be split into two terms. One may be written in terms only of the binary-cluster integral β_2 or strictly the effective binary-cluster one β that is a linear combination of β_2 and a term proportional to the ternary-cluster one β_3 as given by eq 27 of ref 18. The other is a mixed term involving both β and β_3. If we designate them by $A_{3,(2)}$ and A_3^*, respectively, then we have

$$A_3 = A_{3,(2)} + A_3^* \tag{1}$$

where the leading terms of $A_{3,(2)}$ and A_3^* are proportional to β^3 and β_3, respectively.[6,11]

Now, in order to evaluate the effect of chain ends on A_3 as in the case of A_2,[1] we consider the helical wormlike (HW) chain on which $n + 1$ beads are arrayed, where the two end beads are different from the $n - 1$ identical intermediate ones and also from each other in species. For simplicity, we take into account as before[1] the effect only on *single*-contact terms. Then, the leading term of A_3^* involving only a single β_3 and no β is the only one of this kind, since the leading term of $A_{3,(2)}$ is a *triple*-contact term proportional to β^3. In this approximation, eq 1 may be rewritten in the form consistent with eq 23 of ref 1 or eq 14 of ref 4 (eq 8 of ref 5),

$$A_3 = A_{3,(2)}^{(\mathrm{HW})} + \Delta A_3^{*(\mathrm{HW})} + A_{3,(3)}^{(1)} \tag{2}$$

where the superscript (HW) indicates the part of a given quantity without the effect of chain ends, i.e., that quantity for the (fictitious) chain composed of $n + 1$ identical beads, $A_{3,(3)}^{(1)}$ is the leading (single ternary-cluster) term of A_3^*, and $\Delta A_3^{*(\mathrm{HW})}$ is the remaining part of A_3^*.

The term $A_{3,(3)}^{(1)}$ may be written in the form

$$A_{3,(3)}^{(1)} = A_3^0 + A_3^{(\mathrm{E})} \tag{3}$$

where A_3^0 is its part without the effect of chain ends and

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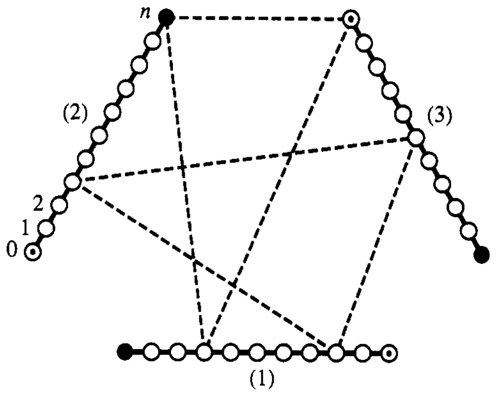

Figure 1. Diagrams for two representative ternary-cluster terms $\beta_{3,000}$ and $\beta_{3,012}$ in the three interacting chains (1), (2), and (3).

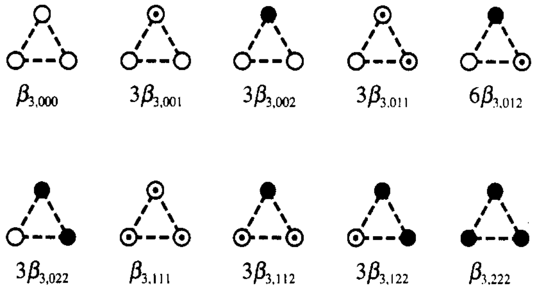

Figure 2. Ten possible kinds of ternary clusters. Each numerical prefactor represents the symmetry factor.

$A_3^{(E)}$ represents the contribution of this effect. It is evident that both of the terms $A_{3,(2)}^{(HW)}$ and $\Delta A_3^{*(HW)}$ are proportional to β and therefore vanish at the Θ temperature, at which β must vanish, so that we have at the Θ temperature

$$A_{3,\Theta} = A_{3,(3)}^{(1)} \tag{4}$$

Thus we evaluate $A_{3,(3)}^{(1)}$. For this purpose, it is convenient to number the $n + 1$ beads in the chain $0, 1, 2, ..., j, ..., n$ from one end to the other and attach the label "0" to the $n - 1$ intermediate beads with $j = 1, 2, ..., n - 1$, the label "1" to the end bead with $j = 0$, and the label "2" to the other end bead with $j = n$, as before.[1] From the general formulation of A_3,[6,19] $A_{3,(3)}^{(1)}$ may then be written in the form

$$A_{3,(3)}^{(1)} = (N_A{}^2/3M^3)\sum\beta_{3,klm} \tag{5}$$

where N_A is Avogadro's number, $\beta_{3,klm}$ is the ternary-cluster integral for the three beads with the labels k, l, and m (=0, 1, 2), and the sum is taken over all possible sets of such three beads, one from one of the three interacting chains (1, 2, 3). It may be expressed as

$$\sum\beta_{3,klm} = -\sum_{i_1}\sum_{i_2}\sum_{i_3}\int \chi_{i_1i_2}\chi_{i_2i_3}\chi_{i_3i_1}\, d\mathbf{R}_{i_1i_2}\, d\mathbf{R}_{i_2i_3}\, d\mathbf{R}_{i_3i_1} \tag{6}$$

where $\chi_{i_1i_2}$ and so on are the χ functions of the distance $\mathbf{R}_{i_1i_2}$ between the i_1th bead of chain 1 and the i_2th bead of chain 2 and so on.[6] Two representative cluster terms $\beta_{3,klm}$ ($\beta_{3,000}$ and $\beta_{3,012}$) are depicted schematically in Figure 1.

Now it is easily seen that there are 10 kinds of ternary clusters, as depicted schematically in Figure 2, where the numerical prefactor of each $\beta_{3,klm}$ represents its symmetry factor. Then eq 6 is reduced to

$$\sum\beta_{3,klm} = (n-1)^3\beta_{3,000} + 3(n-1)^2(\beta_{3,001} + \beta_{3,002}) + 3(n-1)\beta_{3,011} + 6(n-1)\beta_{3,012} + 3(n-1)\beta_{3,022} + \beta_{3,111} + 3\beta_{3,112} + 3\beta_{3,122} + \beta_{3,222} \tag{7}$$

In order to express $A_{3,(3)}^{(1)}$ in the form of eq 3, we define the excess ternary-cluster integrals β_{klm} by

$$\beta_{3,klm} = \beta_3 + \beta_{klm} \tag{8}$$

with

$$\beta_3 \equiv \beta_{3,000} \tag{9}$$

Further, we define three combinations $\beta_{3,1}$, $\beta_{3,2}$, and $\beta_{3,3}$ of β_{klm}s by

$$2\beta_{3,1} = \beta_{001} + \beta_{002}$$

$$4\beta_{3,2} = \beta_{011} + 2\beta_{012} + \beta_{022}$$

$$8\beta_{3,3} = \beta_{111} + 3\beta_{112} + 3\beta_{122} + \beta_{222} \tag{10}$$

These are *effective* excess ternary-cluster integrals associated with the chain end beads.

Thus, if M_0 is the molecular weight of the bead, we finally obtain

$$A_3^0 = N_A{}^2\beta_3/3M_0{}^3 \tag{11}$$

$$A_3^{(E)} = a_{3,1}M^{-1} + a_{3,2}M^{-2} + a_{3,3}M^{-3} \tag{12}$$

where

$$a_{3,1} = 2N_A{}^2\beta_{3,1}/M_0{}^2$$

$$a_{3,2} = 4N_A{}^2\Delta\beta_{3,2}/M_0$$

$$a_{3,3} = (8/3)N_A{}^2\Delta\beta_{3,3} \tag{13}$$

with

$$\Delta\beta_{3,2} = \beta_{3,2} - 2\beta_{3,1}$$

$$\Delta\beta_{3,3} = \beta_{3,3} - 3\beta_{3,2} + 3\beta_{3,1} \tag{14}$$

The term A_3^0, which has often been discussed,[7,8,20] is independent of M, while $A_3^{(E)}$ is of order M^{-1} but eq 12 for it is to be compared with eq 25 of ref 4 (eq 19 of ref 5) for $A_2^{(E)}$.

Experimental Results

The values of A_3 for a-PMMA in acetonitrile at 44.0 °C (Θ) were determined (in the present work) from the Bawn plots[7,21] shown in Figures 4 and 5 of the preceding paper.[5] For a-PS in cyclohexane at 34.5 °C (Θ), A_3 was also determined from the Bawn plots made with the previous light-scattering data,[3] as shown in Figure 3 for the samples with $M_w \leq 1.23 \times 10^3$ and in Figure 4 for those with $M_w \geq 2.31 \times 10^3$, where $S(c_i,c_j)$ is defined by eq 6 of ref 5. Figure 3 also includes the results for the samples OS5 and OS6 obtained in the present work.

All the data for A_3 thus obtained for a-PS and a-PMMA are summarized in Table 1 along with the values of M_w. They are plotted against log M_w in Figure 5, where the filled and unfilled circles represent the values for a-PS and a-PMMA, respectively. The figure also includes the results obtained by Nakamura et al.[8] for a-PS in cyclohexane at Θ (filled circles with pip). The solid curves connect the data points smoothly.

It is seen that our data for a-PS may be smoothly joined to those by Nakamura et al. The values of A_3 for a-PS are almost

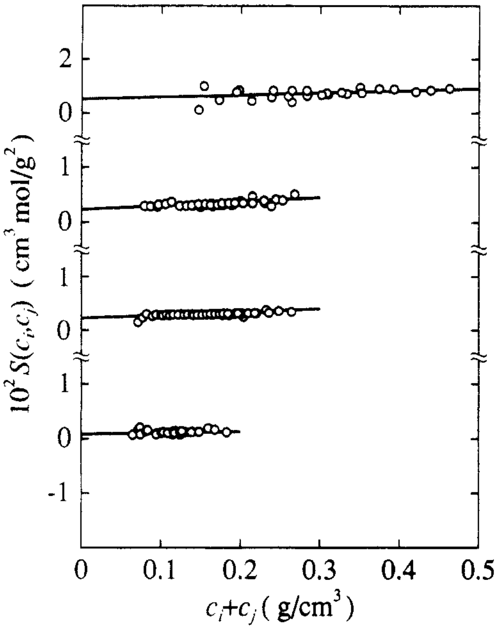

Figure 3. Bawn plots for a-PS in cyclohexane at 34.5 °C (Θ). The samples are OS3, OS5, OS6, and A1000-a from top to bottom.

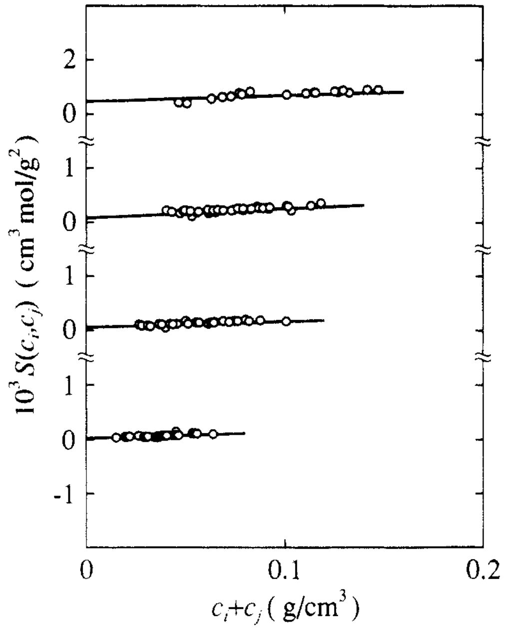

Figure 4. Bawn plots for a-PS in cyclohexane at 34.5 °C (Θ). The samples are A2500-a, A5000-3, F1-2, and F2 from top to bottom.

independent of M_w for $M_w > 10^4$, but it increases monotonically with decreasing M_w for $M_w < 10^4$ with progressively steeper slopes. On the other hand, as M_w is decreased, A_3 of a-PMMA first increases, then passes through a maximum, and finally decreases steeply. For $M_w \gtrsim 10^5$, it seems to level off as in the case of a-PS. It is natural to consider that these molecular-weight dependences of A_3 in the region of small M_w arise from the effects of chain ends, since those of A_2 in the same region of M_w may be well explained similarly, as described previously.[4,5]

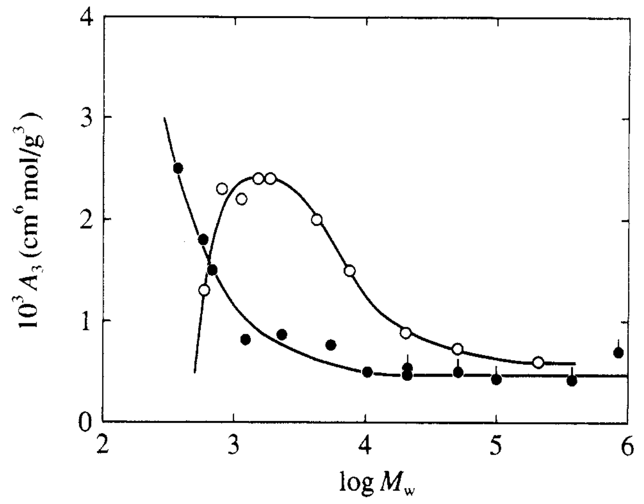

Figure 5. Plots of A_3 against log M_w: (●), a-PS in cyclohexane at 34.5 °C (Θ); (♦), a-PS in cyclohexane at Θ;[8] (○), a-PMMA in acetonitrile at 44.0 °C (Θ). The solid curves connect the data points smoothly.

Table 1. Values of M_w and A_3 for Atactic Oligo- and Polystyrenes in Cyclohexane at 34.5 °C (Θ) and Atactic Oligo- and Poly(methyl methacrylate)s in Acetonitrile at 44.0 °C (Θ)

a-PS/cyclohexane (34.5 °C)			a-PMMA/acetonitrile (44.0 °C)		
sample	$10^{-4}M_w$	10^4A_3 (cm^6 mol/g^3)	sample	$10^{-4}M_w$	10^4A_3 (cm^6 mol/g^3)
OS3	0.0370	25	OM6a	0.0590	13
OS5[a]	0.0578	18	OM8a	0.0800	23
OS6[a]	0.0680	15	OM12	0.113	22
A1000-a	0.123	$8._2$	OM15	0.152	24
A2500-a	0.231	$8._7$	OM18a	0.187	24
A5000-3	0.544	$7._7$	OM42	0.420	21
F1-2	1.03	$5._0$	OM76	0.750	15
F2	2.06	$4._7$	MM2a	2.00	$8._9$
			MM5	5.02	$7._3$
			MM20	20.7	$6._0$

[a] The results for A_3 have been obtained in this work by the same method as described before.[4,5] (The values of A_2 determined simultaneously are 1.15×10^{-3} and 1.12×10^{-3} cm^3 mol/g^2 for OS5 and OS6, respectively.)

Analysis of the Data

We analyze the data for A_3 ($=A_{3,\Theta}$) given in Table 1 by the use of the theory developed in the Theoretical Section. First, it is necessary to determine A_3^0 from the constant value of $A_{3,\Theta}$ in the limit of large M_w, for which $A_{3,\Theta} = A_3^0$, as seen from eqs 3, 4, and 12. The values of A_3^0 thus determined from Figure 5 for $M_w \gtrsim 10^4$ for a-PS and for $M_w \gtrsim 10^5$ for a-PMMA are 4.7×10^{-4} and 5.8×10^{-4} cm^6 mol/g^3, respectively. Then we determine $A_3^{(E)}$ by subtracting A_3^0 from $A_{3,\Theta}$ according to eqs 3 and 4. The values of $A_3^{(E)}M_w$ thus obtained are plotted against M_w^{-1} in Figure 6, where the filled and unfilled circles are the data for a-PS and a-PMMA, respectively. It is seen that $A_3^{(E)}M_w$ is almost independent of M_w for a-PS, for which we may put $a_{3,2} = a_{3,3} = 0$ in eq 12. Thus the horizontal straight line indicated gives the value 0.80 cm^6/g^2 for $a_{3,1}$. In contrast to the results for a-PS, the data points for a-PMMA follow a curve concave upward. Thus, for a-PMMA, we have determined the coefficients $a_{3,1}$, $a_{3,2}$, and $a_{3,3}$ so that the calculated curve of $A_3^{(E)}M_w$ as a function of M_w^{-1} may give a best fit to the data points. The results are $a_{3,1} = 6.6$ cm^6/g^2, $a_{3,2} = -5 \times 10^3$ cm^6/g mol, and $a_{3,3} = 5 \times 10^5$ cm^6/mol^2. The solid curve for a-PMMA in Figure 6 represents the theoretical values calculated with these values of $a_{3,1}$, $a_{3,2}$, and $a_{3,3}$.

From eqs 13 and 14 with the above values of $a_{3,1}$, $a_{3,2}$, and $a_{3,3}$, we can then determine the effective excess ternary-cluster integrals $\beta_{3,1}$, $\beta_{3,2}$, and $\beta_{3,3}$ as defined by eqs 10. The results are $\beta_{3,1} = 1.2 \times 10^{-44}$ cm^6, $\beta_{3,2} = 2.4 \times 10^{-44}$ cm^6, and $\beta_{3,3} = 3.6 \times 10^{-44}$ cm^6 for a-PS and $\beta_{3,1} = 9.1 \times 10^{-44}$ cm^6, $\beta_{3,2} = -1.6 \times 10^{-43}$ cm^6, and $\beta_{3,3} = -2.4 \times 10^{-43}$ cm^6 for a-PMMA, for the repeat unit taken as a single bead. We note that the above values of A_3^0 give 4.4×10^{-45} and

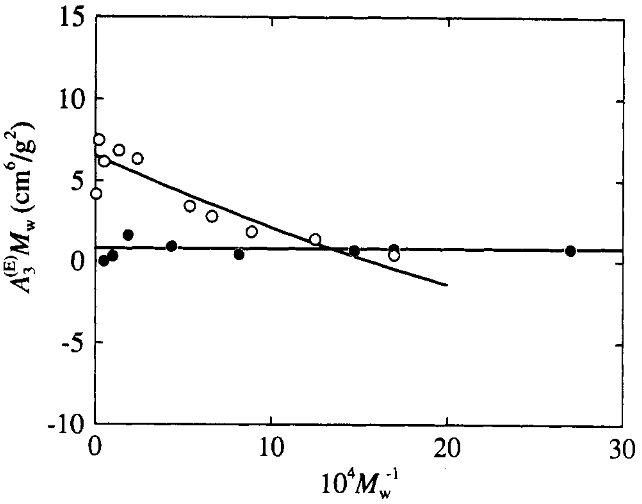

Figure 6. Plots of $A_3^{(E)}M_w$ against M_w^{-1} for a-PS and a-PMMA. The symbols have the same meaning as those in Figure 5. The solid curve for a-PMMA represents the theoretical values calculated from eq 12 (see the text).

4.8×10^{-45} cm^6 for the ternary-cluster integral β_3 per repeat unit for a-PS and a-PMMA, respectively. The above values of $\beta_{3,j}$ ($j = 1, 2, 3$) are of the reasonable order of magnitude since both β_3 and $\beta_{3,j}$ have the dimension of (volume)^2.

In Figure 7 is shown a comparison between theory and experiment for A_3 ($=A_{3,\Theta}$). The filled and unfilled circles are the experimental values for a-PS and a-PMMA, respectively, and the solid curves represent the theoretical values calculated from eqs 3, 4, and 12 with the above values of the ternary-cluster integrals. It is seen that the theory may explain satisfactorily the observed dependence of $A_{3,\Theta}$ on M_w, indicating that it arises definitely from the effect of chain ends.

Conclusion

In light of the recent analysis of A_2 for flexible polymers, we have given a general expression for A_3. It has been explicitly shown that because of possible effects of chain ends, even at the Θ temperature at which the effective binary-cluster integral β vanishes, the nonvanishing part $A_{3,\Theta}$ of A_3, which results from various kinds of ternary-cluster integrals β_3, becomes appreciably dependent on the molecular weight M as M is decreased. This corresponds to the recent theoretical and experimental finding for A_2 that because of the same effects it begins to have finite values dependent on M with decreasing M at the Θ temperature, at which it vanishes for large M. For a-PS in cyclohexane and a-PMMA in acetonitrile, both at Θ, we have confirmed experimentally the above theoretical prediction for $A_{3,\Theta}$. The experimental results show that $A_{3,\Theta}$ becomes dependent on M_w for $M_w \lesssim 10^4$ for a-PS and for $M_w \lesssim 10^5$ for a-PMMA in such a way that it increases monotonically with decreasing M_w for a-PS, while it exhibits a maximum for a-PMMA. The values obtained for the three effective excess ternary-cluster integrals associated with the chain end beads are of the reasonable order of magnitude.

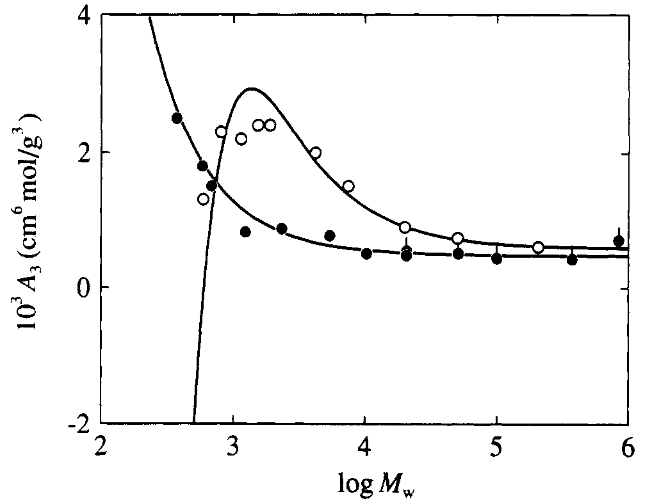

Figure 7. Plots of A_3 ($=A_{3,\Theta}$) against log M_w for a-PS and a-PMMA. The symbols have the same meaning as those in Figure 5. The solid curves represent the theoretical values calculated from eqs 3, 4, and 12 (see the text).

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