3574 *Macromolecules* **1996,** *29,* 3574−3578

Association of Amino-Terminated Polystyrenes. 2. Dynamic Light Scattering of Associating Linear Chains

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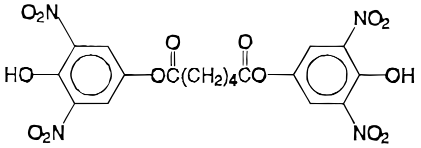
Received March 10, 1995; Revised Manuscript Received January 29, 1996[⊗]

ABSTRACT: Dynamic light scattering was used to study the associating coupling process of amino-terminated polystyrene chains with monofunctional and bifunctional dinitrophenol reagents. The tertiary amino end group and the end group which results from association with monofunctional dinitrophenol were found to have no effect on the solution behavior in good solvents. The interaction with the coupling reagent caused a decrease in the mutual diffusion coefficients D_c with increasing polymer concentration. Translational diffusion coefficients $D_z°(c)$ of the associating polymers at each concentration c with a corresponding molecular weight $M_w(c)$ were determined from D_c and its concentration dependence which is expressed by the k_D parameter. The molecular weight dependence of the k_D parameter was obtained from experimental values of linear polystyrenes in toluene. On the time scale of these experiments, the associates were found to show a diffusion behavior that corresponds to covalently linked chains. Apparently the lifetime of a complex is longer than the measurement time in typical experiments.

1. Introduction

In a preceding paper[1] (I), we reported the association of monofunctional and telechelic polystyrenes (PS) in the good solvent, 1,4-dioxane. In these functionalized polymers, the end groups are tertiary amino groups. From the work of Eisenbach et al.[2−4] and Broze et al.,[5] it is well known how to introduce tertiary amino end groups by anionic polymerization. This can be done either by a termination or by an initiation reaction. Since then, amino-terminated polymers have been the subject of extensive studies of association of polymers. The tertiary amino end group may be converted into a quarternary ammonium salt[6,7] or into a zwitterion[8] which then allows the study of ionomer systems. Such studies were conducted on monofunctional, telechelic, and star branched ionomers.[6,8−11] Recently, sophisticated systems such as zwitterion triblock copolymers were reported by Pispas et al.[12,13] Charlier et al.[14] induce the association of amino-terminated polyisoprenes by complexation of the amino group with transition metal salts. Worsfold[15,16] studied the formation of a dimer which was obtained from an acid−base complex of monofunctional PS with the bifunctional low molecular weight dinitrophenol compound I.

(I)



We extended Worsfold's studies to the association of telechelic and 3-arm star polymers. The advantages of this method of polymer association are the following. (i) As shown previously by static light scattering (SLS), the tertiary amino end group has no detectable effect on the good solvent solution behavior.[1] Thus it is possible to characterize the polymer prior to association. (ii) Association is caused by adding the low molecular weight dinitrophenol compound I. (iii) The junctions consist of pointlike, reversible, well-defined 1:1 complexes of the tertiary amino group and the dinitrophenol derivative. (iv) The complex formation can be followed by means of UV−vis spectroscopy. (v) The complex formation is an equilibrium process, and the equilibrium constant can be measured by UV−vis spectroscopy.[1,15,16] In the preceding study, the properties of the associates as obtained by SLS were considered. An increase in molecular weight with concentration was observed. The experimental results were compared with Flory's theory of linear equilibrium cocondensation.[17,18] Full agreement was found for monofunctional chains. Lower molecular weights than predicted by theory were obtained for telechelics. This finding was explained by ring formation. The number of unimers in the ring fraction could be estimated by the Jacobson−Stockmayer approach[19,20] after extending this theory to incorporate excluded volume effects.[1]

The present paper considers the properties of the associates as observed by dynamic light scattering (DLS). Since the coupling of the chains is reversible, the junctions between the polymers are not permanent but open and close again according to the equilibrium process. This raises the question of whether or not on the time scale of the experiment these complexes behave like corresponding covalently bound chains. DLS is an ideal method for the determination of relaxation-time spectra under thermodynamic equilibrium conditions, i.e., without applying external shear forces.[21]

In the following, we first compare the end-tagged PS with the unfunctionalized PS and then proceed with the DLS data obtained with the associating system.

2. Experimental Section

All experimental procedures are given in paper I and references therein.[1] The polymers of narrow molecular weight distribution were prepared by living anionic polymerization. Tertiary amino groups were introduced either by initiating polymerization[22] of styrene with (3-(dimethylamino)propyl)-lithium (DMAPLi), or by terminating living carbanions with 3-(dimethylamino)propyl chloride (DMAPCL).[5]

SLS and DLS were performed simultaneously by using the ALV 3000 correlation spectrometer system. A Model 2020 krypton ion laser (Spectra Physics) was used as a light source ($\lambda_0 = 647.1$ nm). The time correlation functions (TCF) obtained from DLS were analyzed by the cumulant expansion method.[21,23]

$$\ln g_1(t) = -\Gamma_1 t + (\Gamma_2/2!)t^2 - \Gamma_3/3!t^3 + ... \qquad (1)$$

$g_1(t)$ is the normalized electric field TCF obtained from the measured intensity time correlation function by assuming

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[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1996.

Table 1. Sample Characteristic in Different Solvents: (a) in 1,4-Dioxane; (b) in 1,4-Dioxane with Hydroquinone Monoester; (c) in Toluene[a]

sample	M_w	M_w/M_n	A_2	$D_z°$	R_{eq}/R_h	$k_D°$
MO (a)	5.0	1.1[b]	12.2	10.40	0.85	0 ± 0.5
MO2 (a)	10.0	1.05	8.9	7.35	0.83	0.7 ± 0.3
MO2 (b)	10.0		6.5	7.60	0.83	0 ± 0.5
MO2 (c)	10.0		8.8	18.50	1.10	0.3 ± 0.2
BI1 (a)	17.3	1.3	3.9	5.00	0.68	0.4 ± 0.2
BI1 (b)	17.5		7.8	5.20	0.88	1.1 ± 0.3
BI1 (c)	17.3		8.2	12.10	0.96	0.5 ± 0.2
BI2 (a)	35.0	1.2	6.6	3.50	0.84	0.78
BI2 (b)	34.0		5.5	3.55	0.83	0.81
BI2 (c)	35.0		6.6	7.80	0.91	0.98
BI3 (a)	49.0	1.3	4.5	2.83	0.80	0.85
BI3 (b)	55.0		4.8	2.81	0.86	1.11
BI3 (c)	48.0		6.1	6.21	0.88	1.23

[a] M_w in 10^3 g/mol, M_w/M_n from SEC, A_2 in 10^{-4} mol mL/g^2; $D_z°$ in 10^{-7} cm^2/s. [b] Measured in toluene.

validity of Siegert's relationship.[21,24] In the limit of infinite dilution, the first cumulant Γ_1 is for small chain molecules ($qR_g \ll 1$) related to the z-average of the diffusion coefficient $D_z°$ and the magnitude of the scattering vector q as

$$\Gamma_1 = D_z° q^2 \tag{2}$$

if Γ_1/q^2 is angular independent, which is the case of the present examples. Here R_g denotes the radius of gyration. Thus extrapolation to zero angle was substituted by taking the average of the data at scattering angles θ from 30° to 150°.

The correlation function represents the relaxation-time spectrum as

$$g_1(t) = \int H(\Gamma) \exp(-\Gamma t)\, d\Gamma \tag{3}$$

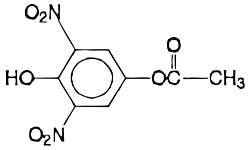
where $H(\Gamma)$ is a distribution function which can be obtained by Laplace inversion of $g_1(t)$ using the program CONTIN.[25] With $\Gamma = Dq^2$, the distribution function $H(\Gamma)$ can be easily converted into the diffusion coefficient distribution.

3. Results and Discussion

3.1. Dilute Solution Behavior of Amino-Terminated PS.

DLS experiments were performed in toluene, 1,4-dioxane, and 1,4-dioxane with an equivalent amount of monofunctional 2,6-dinitrohydroquinone acetic acid ester (II). The results are listed in Table 1.

(II)



These experiments were carried out (i) to compare dilute solution behavior with untagged linear polystyrene chains and (ii) to investigate the influence of the complexed end group on the dynamic solution properties. SLS in good solvents revealed no detectable difference in the osmotic second virial coefficient A_2 between the untagged and amino-terminated PS chains.[1] Apparently, there is no influence of the tertiary amino end group on the static properties of the chains in dilute solution. Similarly, the semidilute solution behavior of the end-tagged PS corresponded to that of the unfunctionalized PS.[22] According to irreversible thermodynamics, the mutual diffusion coefficient D_c contains both thermodynamical and frictional contributions[26]

$$D_c = \frac{k_B T}{f_c} \frac{M_w}{RT} \frac{\partial \pi}{\partial c} \tag{4}$$

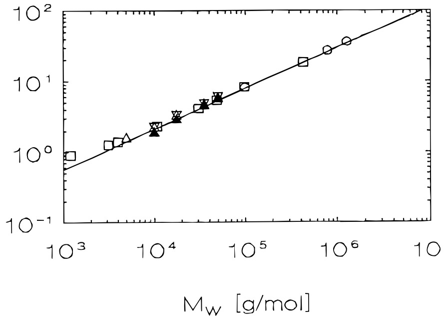


Figure 1. Molecular weight dependence of hydrodynamic radii R_h of amino-terminated and untagged PS in good solvents. The line corresponds to literature data of linear PS in toluene[27] for $M_w > 50 \times 10^3$ g/mol. (○, □) Linear PS in toluene from our laboratory.[28,30,32] Triangles: amino-terminated PS (▲) in toluene, (△) in 1,4-dioxane, and (▽) in 1,4-dioxane with an equimolar amount of monoester II.

where k_B is Boltzmann's constant, T the temperature in kelvin, f_c the concentration-dependent friction coefficient, and π the osmotic pressure. Thus, if in addition to thermodynamic properties also the frictional properties of the amino-terminated PS are the same as for the untagged PS, then the concentration dependence of the mutual diffusion coefficient must be the same as for the untagged PS. The concentration dependence of D_c can often be expressed by a linear relationship

$$D_c = D_z°(1 + k_D c) \tag{5}$$

Extrapolation to concentration $c = 0$ yields the z-average of the translational diffusion coefficient $D_z°$ and the k_D parameter. Using Einstein's relationship, the polymer in solution may be characterized by the hydrodynamic radius R_h of an equivalent hard sphere:

$$R_h = \frac{k_B T}{6\pi \eta_0 D_z°} \tag{6}$$

with η_0 the solvent viscosity. At $T = 20$ °C, one has $\eta_0 = 0.59$ cP for toluene and $\eta_0 = 1.26$ cP for 1,4-dioxane, respectively. Figure 1 shows the molecular weight dependence of the hydrodynamic radii R_h of the amino-terminated PS in the solvent toluene together with the relationship as known from the literature for untagged PS in the same solvent. The line represents a fit to the literature data from 38 well-defined PS samples in toluene.[27] For $M_w > 50 \times 10^3$ g/mol, one has

$$R_h = 1.06 \times 10^{-2} M^{0.575} \quad [\text{nm}] \tag{7}$$

In this study, the molecular weights of the amino-terminated PS were $M_w \le 50 \times 10^3$ g/mol. For a direct comparison, the data at low molecular weight PS are explicitly shown.[28] Clearly, the presence of a tertiary amino group, at either one or both ends of the chain, has no detectable effect on the hydrodynamic radius. The data follow for $M_w > 10 \times 10^3$ g/mol the same power law as given by eq 7. Figure 1 also contains hydrodynamic radii of the amino-terminated PS in 1,4-dioxane (△) and 1,4-dioxane (▽) with an equivalent molar amount of monofunctional hydroquinone ester II. No significant effects are observed by changing the solvent or the nature of the end group. The scatter of the data is within experimental error and the inherent variation of R_h due to the thermodynamic solvent quality.[29]

To demonstrate the concentration dependence of the mutual diffusion coefficient D_c, Figure 2 shows the molecular weight dependence of the normalized k_D

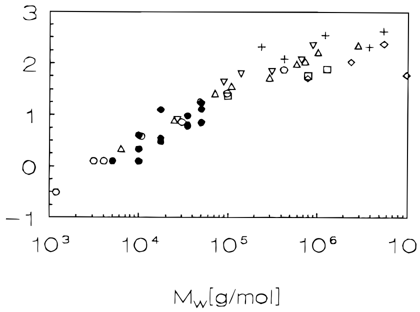


Figure 2. Molecular weight dependence of the $k_D°$ parameter for amino-terminated and untagged polymers: (●) amino-terminated PS in the same solvents as in Figure 1; (○) linear PS in toluene by Huber,[32] (◇) by Bantle,[30] (+) by Varma,[33] and (▽) by Han;[31] (□) Nemoto's data[34] of linear PS in benzene; (△) linear poly(α-methylstyrene) in toluene.[35]

parameter $k_D°$

$$k_D° = \frac{M_w}{V_h N_A} k_D \tag{8}$$

Here V_h is the hydrodynamic volume derived from R_h, and N_A is Avogadro's number. Besides the data of PS in toluene,[30−33] also the data of PS in benzene[34] and of poly(α-methylstyrene) in toluene[35] are included. The scatter of the data is within experimental error, which in the case of low molecular weight polymers ($M_w < 20 \times 10^3$ g/mol) may be in the same order of magnitude as $k_D°$ (see Table 1). However, from the data shown in Figure 2, it is clear that there is no significant difference in the frictional properties of the end-tagged and untagged PS chains. Thus it can be concluded that in good solvents amino-terminated PS's behave as the corresponding untagged linear chains.

Summarizing the results from static and dynamic LS, it can be said that the presence of tertiary amino end groups has no significant effect on the dilute solution behavior of the polymers. The properties of these polymers in solution are dominated by the abundance of the styrene repeating units. This observation is in contrast to polymers bearing ionic groups, which cause a tremendous change in solution behavior, and gelation of telechelic ionomers in organic solvents is achieved.[7,11,12] The weak interaction of the tertiary amino groups in the present systems is of advantage for characterizing the polymers and studying the association process caused by the addition of the low molecular weight coupling reagent I.

3.2. Coupling of Amino-Terminated Polystyrenes. In this section, we consider solutions of amino-terminated PS with an equivalent amount of coupler I; i.e., the ratio r of amino groups to hydroxyl groups was chosen to be $r = 1:1$. All experiments were performed in 1,4-dioxane at 20 °C.

Parts a and b of Figure 3 represent the results from SLS and DLS. Shown are the scattering results from monofunctional PS with and without coupler. The effect of the coupling "reagent" is clearly seen. When extrapolated to zero concentration, monofunctional PS with coupler shows a higher molecular weight and a smaller diffusion coefficient than the polymer alone. Dissociation of the dimeric complex into single chains is observed at low concentrations. Corrections for the effect of the osmotic virial coefficients were performed to obtain the real molecular weights $M_w(c)$ at the actual concentration c (for details, see paper I). For monofunctional PS, the association process could be described with the equilibrium constants derived from UV−vis spectroscopy.

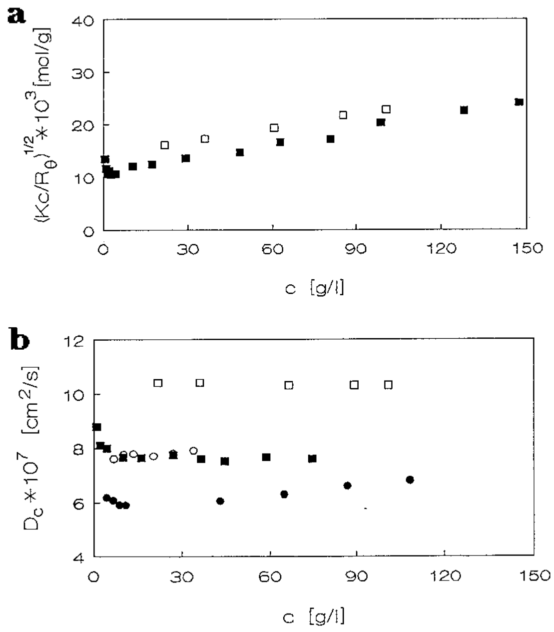


Figure 3. (a) SLS of monofunctional amino-terminated PS MO1 in 1,4-dioxane: (□) without coupler; (■) with coupler. (b) DLS of monofunctional amino-terminated PS in 1,4-dioxane: (□) MO1; (○) MO2. Filled symbols denote solutions with coupler.

Here we are interested in obtaining the translational diffusion coefficient $D_z°$ corresponding to each concentration, which in the following will be denoted as $D_z°(c)$. Accordingly, $D_z°(0)$ is the diffusion coefficient of the unimeric nonassociated polymer chain. Extrapolation to zero polymer concentration is usually performed to extract $D_z°$, but this is not feasible for a system that dissociates on dilution. To derive $D_z°(c)$ from D_c, we make the assumption that for the associating system k_D is the same as for the corresponding covalent polymer of the same molecular weight. This assumption allows with eq 5 the determination of $D_z°(c)$ from one measurement of D_c at a single concentration, if the molecular weight dependence of k_D is known. Several theoretical approximations have been proposed to calculate the molecular weight and temperature dependence of the k_D parameter.[26,35−41] Usually, these calculations express the k_D parameter in terms of the parameter X, which is defined as

$$X = R_{eq}/R_h \tag{9}$$

with

$$R_{eq} = (3M_w^2 A_2/16\pi N_A)^{1/3} \tag{10}$$

Figure 4 shows the same data as in Figure 2 but now plotted against the parameter X. The solid lines represent the theoretical predictions due to Akcasu and Benmouna[36] for polymers in good solvents ($k_D° = 8X^3 + 6X^2$) and the semiempirical approach by Cotts and Selser[35] ($k_D° = 4.8X^3 - 2$). Recently, Douglas[40,41] et al. obtained $k_D° = 4X^3 - 7/4$ based on an approximation that treats the polymer as a droplet with a fluidity similar to that of the surrounding solvent. The scatter of the data, resulting all from linear polystyrenes or poly(α-methylstyrenes) in the good solvent toluene, brings into question the suitability of the parameter X as a proper variable to describe the k_D parameter. Probably the error in the determination of A_2 together with R_h is too high for a reliable prediction. For this reason, we preferred to estimate k_D for the required

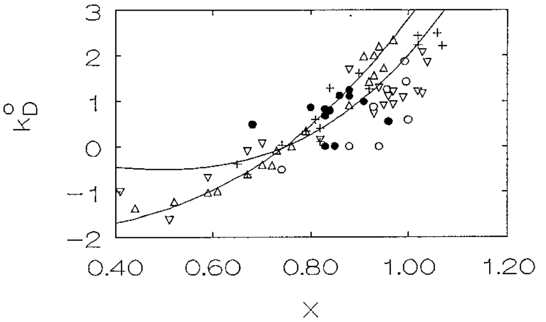


Figure 4. k_D° as a function of the ratio X. (●) Amino-terminated PS in three solvents. Linear PS in toluene: (▽) Han,[31] (○) Huber,[32] (+) Varma.[33] (△) Poly(α-methylstyrene) in the marginal solvent cyclohexane at 50 °C and in the good solvent toluene.[35] The lines correspond to expressions by Cotts[35] and Akcasu,[36] respectively.

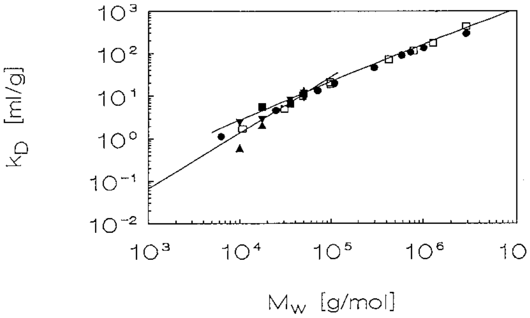


Figure 5. Molecular weight dependence of the k_D parameter of linear polymers: (■, ▲, ▼) amino-terminated PS; (□) linear PS in toluene;[32] (●) poly(α-methylystyrene) in toluene.[35] The lines correspond to eqs 11 and 12.

molecular weight directly from a fit of the experimental data as shown in Figure 5. The data were supplemented by results from higher molecular weight PS in toluene and may be divided into two regions of molecular weight. The following power laws were used to describe the data:

$$k_D = 3.26 \times 10^{-4} M^{0.95} \quad [\text{mL/g}], \qquad M_w > 30 \times 10^3 \tag{11}$$

$$k_D = 7.16 \times 10^{-6} M_w^{1.32} \quad [\text{mL/g}], \qquad M_w < 30 \times 10^3 \tag{12}$$

The molecular weights $M_w(c)$ corresponding to the associates at each concentration were obtained from SLS as previously reported. Having obtained k_D for the associates, the values of D_c could be corrected for $D_z°(c)$ by using eq 5. The results are listed in Table 2 and plotted in Figure 6.

We consider first the association of monofunctional PS. Doubling of molecular weight is the only realistic possibility and was confirmed by analysis of SLS data.[1] Therefore, also the diffusion coefficient should not be lower than that of a corresponding covalent polymer of double molecular weight. This was indeed found and may directly be seen from the raw DLS data (Figure 3b) before correction for k_D. In this molecular weight and concentration region, the corrections are very weak. The associating polymer MO1 (M_w = 5 × 10^3 g/mol) shows a diffusion behavior like the polymer MO2 (M_w = 10 × 10^3 g/mol) without coupler. Addition of the coupler causes polymer MO2 to slow down in dynamics, but no more than a polymer with M_w = 20 × 10^3 g/mol.

The situation is slightly different for the association of the telechelics. Chain extension leads to higher molecular weights and corrections for k_D are necessary.

Table 2. Concentration Dependence of Diffusion Coefficients[a]

c(g/L)	$M_w(c)$	D_c	$k_D(c)$	$D_z°(c)$
(a) MO: $D_z°(0)$ = 10.4 × 10^{-7} cm²/s, $k_D \approx$ 0 mL/g, $M_w(0)$ = 5.0 × 10^3 g/mol				
0.88	7.3	8.80	0.87	8.8
2.17	7.9	8.10	0.96	8.1
4.34	8.6	8.00	1.08	8.0
9.89	9.7	7.65	1.09	7.6
16.31	9.4	7.63	1.21	7.5
27.21	9.3	7.74	1.19	7.5
36.50	9.5	7.60	1.23	7.3
44.70	9.9	7.50	1.30	7.1
58.70	9.7	7.66	1.26	7.1
74.56	10.0	7.60	1.31	6.9
(b) MO2: $D_z°(0)$ = 7.5 × 10^{-7} cm²/s, $k_D \approx$ 2 mL/g, $M_w(0)$ = 10.0 × 10^3 g/mol				
4.32	15.0	6.18	2.24	6.12
6.48	16.6	6.08	2.56	6.00
8.65	17.1	5.91	2.66	5.78
10.81	17.5	5.90	2.74	5.72
43.23	18.4	6.05	2.92	5.37
64.84	19.8	6.30	3.23	5.21
86.84	20.0	6.60	3.27	5.14
108.08	20.0	6.80	3.27	5.02
(c) BI1: $D_z°(0)$ = 5.1 × 10^{-7} cm²/s, $k_D \approx$ 3 mL/g, $M_w(0)$ = 17.5 × 10^3 g/mol				
4.52	22.5	4.40	3.82	4.33
9.04	28.1	3.99	5.12	3.81
13.56	33.0	3.80	6.33	3.50
18.07	36.5	3.81	7.23	3.37
22.59	43.0	3.74	8.97	3.11
(d) BI2: $D_z°(0)$ = 3.5 × 10^{-7} cm²/s, $k_D \approx$ 7 mL/g, $M_w(0)$ = 35.5 × 10^3 g/mol				
2.54	44.2	3.16	7.92	3.10
3.17	56.4	3.01	9.96	2.92
12.68	71.7	2.76	12.50	2.38
19.02	97.8	2.86	16.75	2.17
25.36	115.0	3.01	20.32	1.99
(e) BI3: $D_z°(0)$ = 2.8 × 10^{-7} cm²/s, $k_D \approx$ 10 mL/g, $M_w(0)$ = 50.0 × 10^3 g/mol				
0.54	58.7	2.80	10.35	2.78
1.07	67.9	2.40	11.72	2.37
2.14	68.3	2.40	11.93	2.34
3.21	73.3	2.42	12.76	2.32
4.29	74.7	2.40	12.99	2.27
5.36	80.5	2.35	13.94	2.19
10.70	97.0	2.40	16.62	2.04
21.43	120.0	2.70	20.32	1.88
32.14	160.0	2.85	26.62	1.53

[a] $M_w(c)$ in 10^3 g/mol from SLS derived previously,[1] D_c in 10^{-7} cm²/s from DLS, $k_D(c)$ in mL/g according to $M_w(c)$, $D_z°(c)$ in 10^{-7} cm²/s after correction with $k_D(c)$.

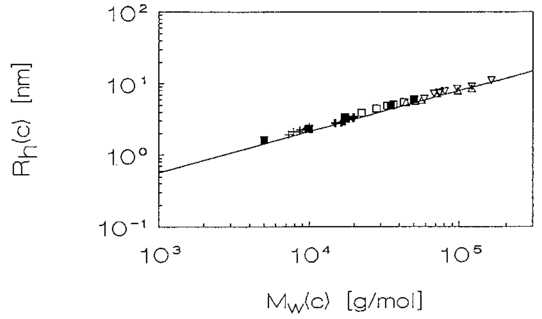


Figure 6. Molecular weight dependence of hydrodynamic radii R_h of covalent linear chains and their associates after addition of coupler: (■) amino-terminated PS without coupler; (×) monofunctional PS MO1 and MO2 with coupler; (box, △, ▽) telechelic PS BI1, BI2, and BI3 with coupler, respectively.

From Figure 6, it can be seen that also this kind of associate behaves like the corresponding covalent linear chains, but now they are exceeding the molecular weight of the dimer. The slope of 0.575 is the same as that found for linear PS in a good solvent.[27] This data treatment neglects the formation of rings, which cer-

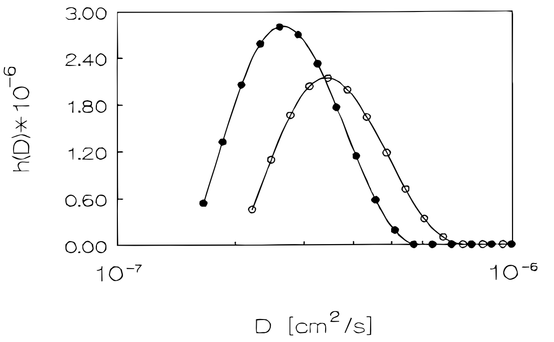


Figure 7. Translational diffusion coefficient distribution *h*(*D*) at two identical concentrations of telechelic PS BI2 (○) without and (●) with coupler.

tainly plays an important role in the association mechanism of the telechelics. However, this shortcoming does not lead to strong deviations, because the hydrodynamic radii of rings and the corresponding linear chains differ by only 10–20%.[42,43] In addition, ring formation is favored at low concentrations, but there the k_D corrections are not very strong. With increasing concentration, the corrections become more relevant but now the probability for ring formation decreases strongly as was shown in paper I. This reduces the error to less than 5%, which is not distinguishable within the experimental error.

4. Conclusions

Analysis of the DLS solution behavior of amino-terminated PS has shown that these polymers behave exactly as their corresponding untagged analogues. There are no detectable contributions from the tertiary amino group to the hydrodynamic radius and the concentration dependence of the mutual diffusion coefficient. These data supplement and confirm the results and conclusions obtained previously by static LS.[1]

Addition of the low molecular weight coupler causes association, and the association could be detected by DLS. After correction of the mutual diffusion coefficient D_c for the intermolecular interactions, the associates were found to show diffusion behavior like the corresponding covalent chains. This means that on the time scale of the experiment these complexes behave like permanent bonds. The same conclusion can be drawn from a CONTIN analysis of the time correlation function. Figure 7 shows the distribution function of diffusion coefficients obtained from 2.5% solutions of polymer BI2 with and without coupler. Addition of coupler caused a shift to smaller diffusion coefficients, which is in agreement with the finding of lower *z*-average diffusion coefficients obtained from the cumulant expansion method. The situation is expected to change when the concentration is increased to the semidilute and concentrated regime. Entanglements then become more important, and the dynamics of the correlation length ξ_h start to dominate the dynamic behavior. Thus, the difference between associating and nonassociating polymers is expected to diminish with increasing concentration as found by Worsfold from viscosity experiments on concentrated solutions of monofunctional PS with coupler.[15]

Acknowledgment. This work was financially supported by the Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich 60. G.M. thanks the Alexander von Humboldt-Stiftung for a Feodor Lynen fellowship. We also thank Dr. Jack Douglas for many stimulating discussions.

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MA950315C