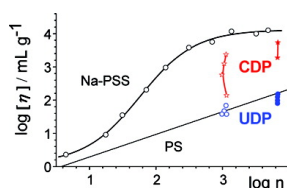


Branched versus Linear Polyelectrolytes: Intrinsic Viscosities of Peripherally Charged Dendronized Poly(methyl methacrylate)s and of Their Uncharged Analogues

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n: number of segments
CDP: charged dendronized polymers/water
UDP: uncharged dendronized polymers/chloroform
Na-PSS: Na-polystyrene sulfonic acid/water
PS: polystyrene/ethylbenzene

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Branched versus Linear Polyelectrolytes: Intrinsic Viscosities of Peripherically Charged Dendronized Poly(methyl methacrylate)s and of Their Uncharged Analogues

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ABSTRACT: Viscosities of dilute solutions were measured for four generations of peripherically charged dendronized poly(methyl methacrylate)s (CDPs) of two different chain lengths in water (no salt added) and of their uncharged analogues (UCPs) in chloroform. In all cases it was possible to describe $\ln(\eta_{\text{solution}}/\eta_{\text{solvent}})$ as a function of polymer concentration by two adjustable parameters: a hydrodynamic interaction parameter B and $[\eta]$, the intrinsic viscosity of the polymer. The $[\eta]$ values for the first generation of polyelectrolytes are markedly lower (given number of monomeric units) than that of aqueous solutions of Na-polystyrene sulfonate reported earlier, despite the fact that each monomeric unit is much larger and bears two charges instead of one; as the number of generation rises, $[\eta]$ falls markedly for the CDPs as well as for the UCPs, where the effect is considerably more pronounced for the polyelectrolyte. The increase in molar mass M associated with the addition of dendrons leads to a maximum in the molar hydrodynamic volume $[\eta]M$ for the second generation of the CDP; in case of the UCPs this volume increases steadily. The interaction parameter B is normally positive but may for the higher generations become negative, corresponding to a more than exponential augmentation of η with polymer concentration. A consistent description of the findings is presented in terms of intra- and intermolecular interactions between the -NH and -O- groups of the dendrons and the distances of the charges from the polymer backbone.

1. Introduction

Dendronized polymers have a linear backbone in which a dendron of a certain generation is attached to every repeat unit.¹ The steric bulk generated this way is in direct proximity to the backbone, causing it to stretch and partially uncoil, and leads to an increased persistence length.² Terminally charged representatives have been studied both in solution and bulk and were found to exhibit unusual behavior. For example, in aqueous solution positively charged third and fourth generation dendronized polymers can form duplex structures in which individual chains are folded back on themselves;^{3a} at higher concentration duplexes of different strands were found to be integral parts of networks.^{3b} It was also shown that dsDNA winds around positively charged dendronized polymers to give defined hybrid aggregates.^{3c} If put together with oppositely charged surfactants, finally, these highly branched polymers give rise to a rich variety of partially unique bulk phases.⁴ Considering these properties, it seems that the charged versions of dendronized polymers are polyelectrolytes that differ from their well-known nonbranched counterparts. In order to explore this seeming difference, we have started to explore the viscosity behavior of neutral and charged dendronized polymers and compare it to that of linear polystyrylsulfonate.

Well founded information on the intrinsic viscosities of polyelectrolytes in pure water is still rather scarce, even for simple linear polymers, above all because of the fundamental problems with the normally used Huggins relation,⁵ which leads to a zero-divided-by-zero situation upon the extrapolation to

infinite dilution. A more systematic study, using a different approach,⁶ has only recently been initiated.⁷ The central variables for such an investigation are on the polymer side: the numbers of charges per monomeric unit (including "copolymers" of charged and neutral groups), the distance of these charges from the polymer backbone, and the numbers n of the monomers linked to a polymer. In case of the present dendronized polymers the first generation bears two charges, and this number is doubled by each further addition of a dendron, i.e. reaches a maximum of sixteen charges for the fourth generations under investigation; the n values under investigation were approximately 1000 and 6000, respectively. The next decisive parameters come in with the choice of the solvent and its interaction with the sometimes chemically rather dissimilar groups of the monomeric units. This thermodynamic aspect becomes particularly important with large dendrons, where favorable or unfavorable interactions govern the probability of contact formation between the polymer segments and solvent molecules. In the case of dendronized polymers and special interactions between the different groups comprising the monomeric units, it must be expected that the fraction of intramolecular and intermolecular contacts between these entities will vary with polymer concentration and consequently influence the flow behavior. In case of the peripherically charged dendronized polymers, a further aspect arises, namely the relative importance of Coulombic and non-Coulombic interactions.

By means of the work presented here, we wanted to first obtain information concerning the role of the different variables introduced above. In particular we wanted to investigate to what extent the intrinsic viscosities and interaction parameters B of the CDPs in pure water differ from that of Na-PSS in the same solvent and how the addition of further generations influences the results. In an attempt to separate the effects that are caused by electric charges from those resulting from interactions

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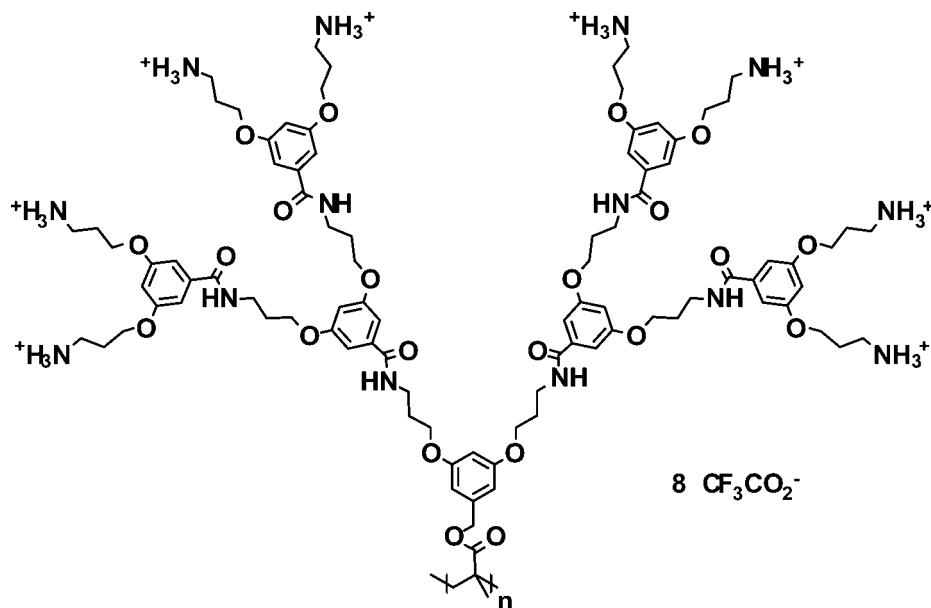


Figure 1. Third generation polymer as an example for the structure of the CDPs; n is the number of monomeric units. Upon the addition of a further generation, the number of charges doubles. In case of the uncharged samples UDP, the end groups NH_3^+ are replaced by NHBoc .

Table 1. Characteristic Data for Different CDP Samples^a

sample	M_n kg/mol	n	PDI	25 °C		B	error	50 °C		B	error
				$[\eta]$ mL/g	error			$[\eta]$ mL/g	error		
1L	360	1 130	1.42	2 366	6	0.99	0.10	4 137	42	0.87	0.026
1H	2210	6820	3.22	5 414	12	0.42	0.005	8 200	73	0.48	0.013
2L	880	1 060	1.53	1 253	6	0.66	0.28	2 305	102	0.76	0.137
2H	5 540	6 730	1.60	1 901	4	1.71	0.11	2 930	78	1.25	0.024
3L	1 790	980	1.60	578	3	-4.21	0.91	1 265	26	1.41	0.20
4L	4 410	1 150	1.74	139	4	-1.82	0.26	314	18	0.95	0.25

^a The numbers of the sample designation give the generation of the dendrimer, L and H state, whether it is a low or a high molecular weight product; n is the number of monomeric units and PDI is the polydispersity index. Also reported are their intrinsic viscosities and the viscometric interaction parameters B measured in water, as obtained from the primary data according to eq 6.

between the bulky side groups of the dendronized polymers, we have also determined $[\eta]$ and B for solutions of the uncharged analogous UDPs in chloroform. The well-known behavior of ordinary vinyl polymers in organic solvents was in all cases a common reference point.

2. Experimental Section

Polymers. Four generations of two types of dendronized poly(methyl methacrylate)s were studied. Figure 1 shows the structure of the third generation of the peripherally charged dendronized polymer (CDP). Also studied were the corresponding uncharged products (UDP), where NH_3^+ was replaced by $\text{NH}\text{-tert-butoxycarbonyl}$ groups. The polymers were prepared on a multigram scale according to the attach-to route⁸ by starting from deprotected first generation dendronized polymers with different numbers of repeat units (1000 and 6000). To these, first generation dendrons were successively attached by active ester chemistry until the desired generation was achieved. The perfection of this attachment chemistry was assessed by a strict mass balance, NMR spectroscopy, and the data from elemental analysis. Gel permeation chromatography was carried out on a PL-GPC 220 instrument with 2 \times PL-Gel Mix-B LS column set (2 \times 30 cm) equipped with refractive index (RI), viscosity, and light scattering (LS; 15° and 90° angles) detectors, and DMF (containing 1 g/L LiBr) as eluent at 45 °C. The universal calibration of the instrument was performed with poly(methyl methacrylate) standards in the range of M_p = 2680 to 3900000 (Polymer Laboratories Ltd., UK). The data confirmed the increasing molar mass and yielded the polydispersity indices reported in Table 1. Deprotection was done with neat trifluoroacetic acid, and the resulting CDPs were dialyzed against Millipore water in order to remove any acid contaminations. The polymers were freeze-dried before use.

Table 1 specifies the molar masses and number of polymer segments of the different generations of the peripherally charged dendronized PMMA samples. Furthermore, it collects the results of all viscometric measurements performed with the aqueous solutions of the different CDP samples.

The time required to prepare homogeneous aqueous solutions of the CDPs depends strongly on the number of generations and on the molar mass of the different products: 1L and 2L are completely soluble within 5–6 h, whereas 1H and 2H require a full day. With 4L it was also necessary to store the dry sample in the refrigerator to avoid changes with time. Of the third and fourth generation, only the low molecular weight samples are soluble, approximately two days being required to reach homogeneity.

All samples of UDP are readily soluble, in contrast to CDP, independent of the number of generations, though the dissolution of the high generation and high molar mass UDPs in solvents such as chloroform may require a few days time to complete; the characteristic data for this polymer and the viscometric results for their solutions in chloroform are presented in Table 2. It appears worthwhile to mention that the conventional data evaluation according to Huggins (eq 3) and the procedure implemented for polyelectrolyte solutions⁶ (eq 6) yield almost identical intrinsic viscosities. The former values are on the average 3% lower than the latter. However, the differences in the corresponding viscometric interaction parameters, k_H and B (cf. eq 8), are considerable larger.

Viscometry. All experiments were performed at 25 °C using Ubbelohde capillary viscometers for dilution sequences of type Oa with a capillary diameter of 0.53 mm, in combination with AVS 310 (Schott, Mainz, Germany). Hagenbach corrections were applied whenever necessary. All samples were freed of dust by means of filters with a pore diameter of 0.45 μm (Spartan 30/B, Schleicher

Table 2. Characteristic Data for Different Generations of UDPs^a

sample designation	M_n , kg/mol	$[\eta]_{\text{CHCl}_3}$, mL/g, eq 6	error	B	error	$[\eta]_{\text{H}_2\text{O}}^{\text{CDP}}/[\eta]_{\text{CHCl}_3}^{\text{UDP}}$
1L ⁰	520	68.8	1.6	0.138	0.042	34.4
1H ⁰	3560	152.2	5.9	0.078	0.062	35.6
2L ⁰	1220	47.0	0.9	0.210	0.050	26.7
2H ⁰	8230	123.6	1.9	0.090	0.030	15.4
3L ⁰	2620	38.2	0.6	-0.212	0.046	15.1
3H ⁰	16800	98.2	2.9	-0.285	0.070	—
4L ⁰	5430	37.4	0.6	0.085	0.052	3.7
4H ⁰	40600	80.1	2.0	-0.096	0.077	—

^a The uncharged samples are marked by superscript zero. The viscosity measurements were performed at 25 °C using chloroform as the solvent. Also shown are the ratios of the intrinsic viscosities of the charged and the uncharged polymers.

& Schuell, Dassel, Germany). Only freshly prepared samples were used.

3. Theoretical Background

The intrinsic viscosity $[\eta]$ of a certain polymer in a given solvent can be obtained in two alternative ways from η , the viscosities measured at a given polymer concentration c (mass/volume), in comparison with the η_s , the viscosity of the solvent at sufficiently low shear rates $\dot{\gamma}$. One is the traditional extrapolation according to Huggins:⁵

$$\lim_{\substack{c \rightarrow 0 \\ \dot{\gamma} \rightarrow 0}} \frac{\eta - \eta_s}{c} = \lim_{\substack{c \rightarrow 0 \\ \dot{\gamma} \rightarrow 0}} \frac{\eta_{\text{spec}}}{c} \equiv [\eta] \quad (1)$$

A series expansion of η_{spec} with respect to the dimensionless reduced concentration \tilde{c}

$$\tilde{c} = [\eta]c \quad (2)$$

yields the usually employed Huggins relation

$$\frac{\eta_{\text{spec}}}{c} = [\eta](1 + k_H c [\eta] + \dots) \quad (3)$$

where k_H is the Huggins constant; the extrapolation to infinite dilution is in this case complicated by a “zero-divided-by-zero” situation.

Alternatively, intrinsic viscosities can be determined from the composition dependence of the relative viscosity⁶ $\eta_{\text{rel}} (= \eta_{\text{solution}}/\eta_{\text{solvent}})$ by plotting the natural logarithm of this quantity as a function of c . The slope of this dependence at an arbitrary composition of the solutions yields $\{\eta\}$, the specific hydrodynamic volume of the polymer

$$\left(\frac{\partial \ln \eta}{\partial c} \right)_{T, p, \dot{\gamma}} = \{\eta\} \quad (4)$$

and its limiting value for $c \rightarrow 0$ gives access to $[\eta]$

$$\lim_{\substack{c \rightarrow 0 \\ \dot{\gamma} \rightarrow 0}} \{\eta\} = [\eta] \quad (5)$$

This procedure avoids the “zero-divided-by-zero” situation and enables a reliable determination of $[\eta]$ directly from the initial slope of the plots $\ln \eta_{\text{rel}}$ versus c . The following expression represents the experimental observations for charged and for uncharged polymers very accurately. The quantitative description of the only polyelectrolyte solutions studied in detail so far⁷ requires one parameter more than the Huggins equation, namely $[\eta]^*$; for ordinary uncharged polymers this parameter is found to be zero.

$$\ln \eta_{\text{rel}} = \frac{c[\eta] + Bc^2[\eta][\eta]^*}{1 + Bc[\eta]} \quad (6)$$

B corresponds to the Huggins constant and $[\eta]$ accounts for the observation that the specific hydrodynamic volume may for polyelectrolytes become constant within a certain composition

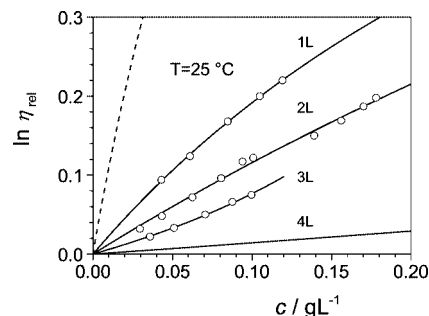


Figure 2. Evaluation of the viscometric data according to eq 6 for the lower molecular weight samples of the dendrimer generations 1–3 at 25 °C. Also shown is the curve for generation 4, taken from Figure 4. The dotted line represents the data for the linear polyelectrolyte NaPSS with 1370 monomeric units.⁷

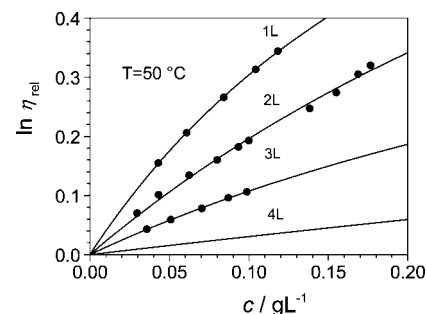


Figure 3. Evaluation of the viscometric data according to eq 6 for the lower molecular weight samples of the dendrimer generations 1–3 at 50 °C. Also shown is the curve for generation 4, taken from Figure 4.

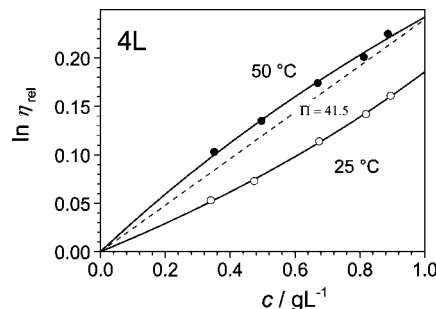


Figure 4. Evaluation of the viscometric data (25 and 50 °C) according to eq 6 for the fourth generation of the dendrimer. The broken line indicates that the concentration dependence of $\ln \eta_{\text{rel}}$ becomes linear at the Π temperature (cf. Discussion). This particular behavior implies that $\{\eta\}$ becomes equal to $[\eta]$ within the composition range under investigation.

range. Equations 4 and 6 yield the following expression for the variation of the specific hydrodynamic volume $\{\eta\}$ with the reduced polymer concentration \tilde{c}

$$\frac{\{\eta\}}{[\eta]} = \frac{1 + 2Br\tilde{c} + B^2r\tilde{c}^2}{1 + 2B\tilde{c} + B^2\tilde{c}^2} \quad \text{where } r = \frac{[\eta]^*}{[\eta]} \quad (7)$$

4. Results and Discussion

The following paragraphs collect the entire experimental information in terms of the composition dependence of the relative viscosity, $\eta_{\text{rel}} = \eta_{\text{solution}}/\eta_{\text{solvent}}$, in graphs of $\ln \eta_{\text{rel}}$ as a function of polymer concentration c (mass per volume) according to eq 6. The limiting slope of these dependencies for $c \rightarrow 0$ yields $[\eta]$, and the curvature reflects the hydrodynamic interaction parameter B .

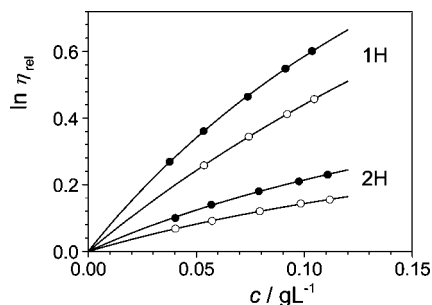


Figure 5. Evaluation of the viscometric data (open symbols: 25 °C; full symbols: 50 °C) according to eq 6 for the high molecular weight samples of the generations 1 and 2.

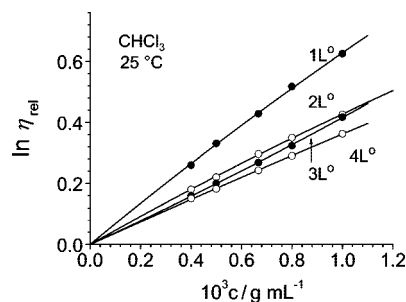


Figure 6. Evaluation of the viscometric data for solutions of the lower molecular weight samples of the UDP in chloroform according to eq 6 at 25 °C.

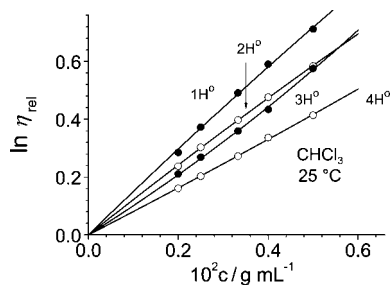


Figure 7. Evaluation of the viscometric data for solutions of the higher molecular weight samples of the UDP in chloroform according to eq 6 at 25 °C.

The most striking observation of the present study concerns the fact that the concentration dependence of the viscosity of aqueous solutions of CDP can be described by only two system-specific parameters, like that of the solutions of UCP in chloroform, namely $[\eta]$ and B . This outcome is surprising in view of the results obtained for aqueous solutions of the sodium salt of polystyrene sulfonic acid (Na-PSS), where a nonzero parameter $[\eta]^*$ is required for a quantitative description of the data. The most likely explanation for the different behavior of the two types of polyelectrolyte lies in the larger distance of the charges from the polymer backbone in case of the CDPs. This reasoning is backed by fact that the dissimilarities between the intrinsic viscosities of CDP in water and that of UDP in chloroform decrease considerably upon the addition of a further generation.

Before embarking on a more detailed discussion of viscometric interaction coefficients and intrinsic viscosities it is advisable to compare possible differences in the data evaluation according to eqs (6) and (3). To this end we plot the data for the sample 3L and 25 °C (cf. Figure 2) also in a Huggins plot in Figure 8.

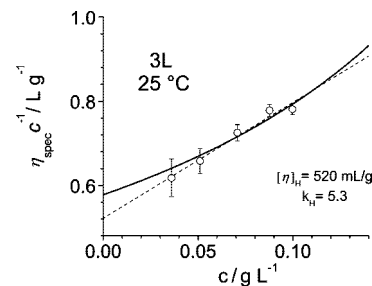


Figure 8. Huggins plot for 3L and 25 °C. To calculate the error bars it was assumed that the uncertainty in the flow times through the capillary is $\pm 0.1\%$. The full line is drawn according to eq 6 using the parameters of Table 1. The k_H value of 5.3, resulting from this graph, translates to $B = -4.2$ according to eq 8.

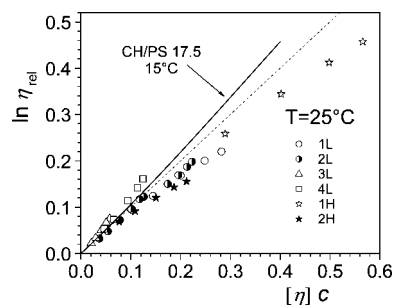


Figure 9. Dependence of $\ln \eta_{rel}$ on the reduced polymer concentration \tilde{c} at 25 °C for all CDP samples. The broken line represents the diagonal ($B = 0$; eq 6); the full line stands for cyclohexane/polystyrene 17.5 kg/mol at 15 °C, i.e. for conditions which are considerably worse than at the Θ temperature of that system.⁹

The superiority of the evaluation according to eq 6 as compared with eq 3 becomes immediately obvious. The pronounced increase in experimental uncertainties upon the approach of the infinitely dilute state makes the intrinsic viscosities obtained for polyelectrolytes in Huggins plots rather incorrect. In all graphs of the last section ($\ln \eta_{rel}$ versus c ; eq 6) the error bars are smaller than the size of the symbols and remain constant within the entire composition range.

In order to be able to compare the hydrodynamic interaction parameters k_H (obtained from eq 3) with the B values (resulting from eq 6) we equate the corresponding expressions for $\ln \eta_{rel}$ and expand both sides in the Taylor series with respect to the reduced polymer concentration ($[\eta]c = \tilde{c}$) up to the quadratic term. In this manner one obtains the following interrelation

$$k_H = \frac{1}{2} - B \quad (8)$$

which only holds true for the range of pair interactions between the solute. The particular situation of $B = 0$ (no curvature in $\ln \eta_{rel}$ versus c) consequently translates to $k_H = 0.5$. However, the equivalence of the hydrodynamic interaction parameters formulated in eq 8 already fails at approximately $\tilde{c} = 0.25$ in Huggins plots and at $\tilde{c} = 0.50$ in plots of $\ln \eta_{rel}$ versus c . A comparison of the k_H values resulting from the primary data measured within a given compositions range in Huggins plots with the B values collected in Table 1 demonstrates that eq 8 is well obeyed in some cases, whereas not even the sign results correctly in others.

Composition Dependence of Viscosities. Figure 9 gives a joint representation of the data obtained at 25 °C for the aqueous solutions of CDPs (cf. Figure 2 and Figure 4 to Figure 7) in terms of *reduced* polymer concentrations. The initial slopes of these dependencies (the independent variable being $[\eta]c$) is unity in all cases as postulated by eq 6. Whether the individual curves

bend downward or upward is determined by the sign of B . The corresponding graphs for 50 °C (Figure 3) and for the solutions of the UDPs in chloroform look very similar to Figure 9.

B is positive for almost all uncharged polymers, which means that the relative increase in viscosity slows down as the polymer concentration rises. This behavior is typical for thermodynamically favorable solvents. Under these conditions the polymer coils shrink upon an augmentation of c (cf. eq 7) because of the preference of contacts between solvent molecules and polymer segments. The pronounced coil expansion caused by these favorable interactions at high dilution no longer appears at larger concentrations, because the solvent molecules formerly taken from a reservoir of pure solvent would now have to be taken out from other polymer coils. Only for thermodynamically very unfavorable conditions,⁹ such as in the case of the system cyclohexane/polystyrene $M = 17.5$ kg/mol at 15 °C, i.e. well below the Θ temperature, k_H may become uncommonly large, namely 1.12, and translates to negative B values (cf. eq 8). The reason for the corresponding strong augmentation of $\ln \eta_{\text{rel}}$ with rising polymer concentration lies in the special thermodynamic situation leading to a pronounced preference of intersegmental contacts over contacts between segments and solvent molecules; under these conditions the coils are considerably shrunken below their unperturbed dimensions in the isolated state and expand upon an increase in c .

In case of the CDPs, the hydrodynamic interaction parameter B is positive for the first and second generation, whereas $B < 0$ for the low molecular weight samples of the third and fourth generation (the higher molecular samples are insoluble). This observation signifies that the third and the fourth generation of the ionized dendrimers behave in terms of hydrodynamic interaction like uncharged polymers in an extremely unfavorable solvent.

For a better understanding of the physical meaning of the parameter B in the case of charged macromolecules, we split this quantity up into two parts, one comprising all effects of Coulombic interactions and another part containing interactions that are also present in uncharged polymer, according to the relation

$$B = B_{\text{Coulomb}} + B_{\text{non-Coulomb}} \quad (9)$$

Along this line of action it is possible to discuss the change in the sign of B with temperature as observed with the samples 3L and 4L (cf. Figures 2–4). Based on the hypothesis that the non-Coulombic part of B is negative at 25 °C, as with the system cyclohexane/polystyrene, whereas the Coulombic part is positive, we can infer that this inversion of B may be a consequence of a predominance of the non-Coulombic contribution at low temperature and of the Coulombic contribution at high temperatures. According to these considerations there should exist a characteristic temperature Π , where $B = 0$ because of an exact compensation of opposite effects, such as in the case of Θ temperatures, where the compensation of entropic and enthalpic contributions leads to an ideal behavior of the mixture. In the present viscometric analogue this ideality means that the specific hydrodynamic volume becomes independent of composition and identical with $[\eta]$ in the composition range of interest (cf. eq 7) according to

$$\{\eta\} = [\eta] \text{ if } B = [\eta]' = 0 \quad (10)$$

In Figure 9 this situation corresponds to the dotted diagonal. In default of more detailed information concerning temperature influences, we assume a linear dependence for the small T -interval of interest; under this premise $\{\eta\} = [\eta]$ is reached at $\Pi = 49.0$ °C for the sample 3L and at $\Pi = 41.5$ °C for the sample 4L.

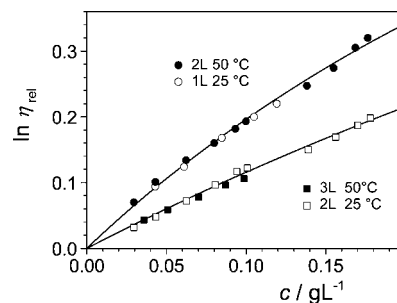


Figure 10. Composition dependence of $\ln \eta_{\text{rel}}$ for the samples 1L, 2L, and 3L at two different temperatures.

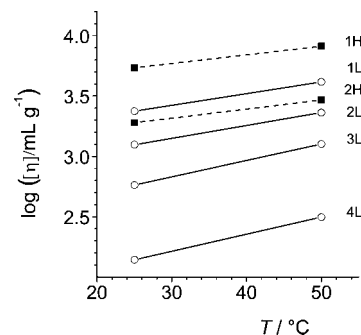


Figure 11. Temperature influences on the intrinsic viscosities of the different CDP samples in water.

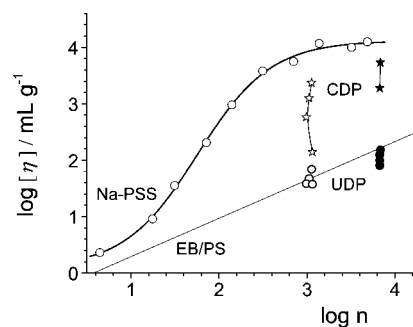


Figure 12. Double logarithmic plot of $[\eta]$ as a function of n , the number of polymer segments, for aqueous solutions of the different generations of CDP (charged dendronized PMMA) in water and that of UDP in chloroform. As the number of generations rises, the $[\eta]$ fall. For the sake of comparison, the results for aqueous solutions of Na-PSS⁷ and for the system ethyl benzene/polystyrene¹⁰ are also shown in this graph. All data refer to 25 °C.

Further evidence of the important role the temperature plays for the viscometric behavior is provided by the observation that the composition dependence of η_{rel} of 1L at 25 °C becomes identical with that of 2L at 50 °C and correspondingly that of 2L at 25 °C with that of 3L at 50 °C as depicted in Figure 10. The exact match of the curves is certainly accidental; however, it indicates that it should be possible to establish a master curve for the influences of the polymer generations and of temperature.

Intrinsic Viscosities. For the CDPs, one obtains markedly lower $[\eta]$ values than for aqueous solutions of Na-PSS of comparable chain length or molar mass (cf. Figure 12 and Figure 13). This behavior is probably due to the fact that the distances of the individual charges from the polymer backbone are much larger in the former than in the latter case. This fact should reduce the repulsion between like charges and consequently the extension of individual polyelectrolyte chains caused by Coulomb interactions. How the intrinsic viscosities vary with temperature is shown in Figure 11. This graph manifests that $[\eta]$ invariably increases with rising temperature. In the case of

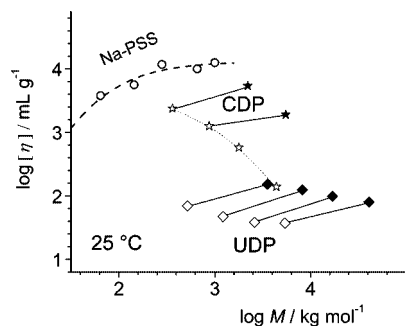


Figure 13. Kuhn–Mark–Houwink plot demonstrating how the intrinsic viscosities of the dendronized PMMA sample vary with molar mass M for a given generation. Full lines connect points belonging to the same generation; the dotted line joins the lower molecular weight samples of the different generations for the system CDP/water. Also included in this graph are the dependencies for the system Na-PSS/water and for UDP/chloroform. All data refer to 25 °C.

uncharged polymers such an observation constitutes a sign of an unfavorable thermodynamic quality of the solvent, caused by endothermal mixing (strictly speaking dilution). For the charged CDPs, this result can be taken as a further indication of a negative non-Coulombic part of B , caused by a thermodynamic preference of intersegmental contacts, the Coulombic part of B being positive due to electrostatic interactions trying to minimize the number of intersegmental contacts.

There exist two different ways to compare the intrinsic viscosities of the CDPs with that of other polymers and to discuss the differences between the different generations of the CDPs. One can either choose the number of polymer segments, n , as the independent variable (Figure 12) or select the molar mass of the polymers for that purpose (Figure 13). The former alternative compares the data at constant contour length, whereas the latter accounts for the fact that the mass per repeating unit increases more than an order of magnitude as one goes from the first to the fourth generation.

Figure 12 demonstrates that the intrinsic viscosities of the CDPs are for constant n located approximately in the middle between the markedly larger values of Na-PSS and the considerably lower $[\eta]$ values measured for solutions of polystyrene in ethyl benzene. This graph also displays very clearly how the intrinsic viscosities decrease upon each further addition of a generation to the monomer, keeping the degree of polymerization constant. Another interesting feature concerns the position of the corresponding data for the UDPs: The effect of the generations is qualitatively the same but considerably less pronounced. Furthermore the $[\eta]$ values are not fundamentally different from that of the solutions of ordinary linear vinyl polymers in organic solvents.

Figure 13 presents the evaluation according to the well-known Kuhn–Mark–Houwink relation

$$\log[\eta] = K + \alpha \log M \quad (11)$$

This equation describes the molecular weight dependence of the intrinsic viscosities (within a limited range) by means of two adjustable parameters. For uncharged polymers, α increases as the solvent becomes thermodynamically more favorable. From a graph of this kind it is possible to estimate to which extent the addition of bulky side groups to the polymer backbone changes α . Despite the fact that only two samples of different M were available and only for the first and for the second generation, one can obtain some information concerning α . For the first generation, the value is 0.35 and for the second 0.22. According to these data, one can tentatively infer that the exponent decreases upon the addition of a second generation. This conclusion would fit well into the general picture and

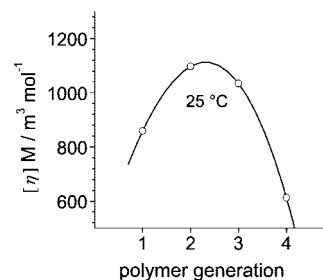


Figure 14. Molar hydrodynamic volume of isolated coils of the different low molecular weight samples ($n \approx 1000$) of CDPs at 25 °C. The curve is a guide for the eye only and calculated according to a quadratic function.

the observation that the higher molecular weight samples of the third and fourth generation are no longer soluble in water. The question remains, however, why the CDPs are soluble at all, knowing that such low α values were never observed with uncharged polymers so far. One might speculate that this particular behavior results from the electrostatic repulsions leading to a large expansion of the polymer coils and consequently to anomalously high entropies of mixing. This reasoning is in agreement with the observation that a deterioration of solvent power with increasing number of generations, as observed for CDPs, is absent for the uncharged samples and all that the α values for the system chloroform/UDP are close to 0.5 (typical for theta conditions).

In order to obtain a more illustrative notion of the particularities of isolated coils of charged macromolecules and of the effects of more or less bulky side groups, we compare Φ_o , the average volume fractions of the polymer segments within the realm of such a particle, and its molar volume $[\eta]M$ with the corresponding data for uncharged polymers. For Φ_o , we can write¹¹

$$\Phi_o \approx \frac{1}{\rho_{\text{polymer}}[\eta]} \quad (12)$$

In view of the large effects discussed here, we perform this comparison with an estimated average polymer density of 1.5 g/mL. In this manner one ends up with approximately 1.5 vol% of segments in an isolated coil of an uncharged polymer of 1000 monomeric units. Because of electrostatic expansion, this value decreases by more than 2 orders of magnitude to approximately 0.01 vol% for a corresponding Na-PSS molecule. For CDPs, the data fall between these extremes and increase from 0.03 (first generation) to 0.45 vol% (fourth generation).

The hydrodynamically efficient spatial extension of isolated macromolecules is quantified by the molar volume $[\eta]M$. It appears particularly interesting to check how this quantity changes upon the addition of further generations of the CDPs. According to the results shown in Figure 14, the coil dimensions increase expectedly as one goes from the first to the second generation; however, thereafter they fall markedly. This effect is probably due to the increasing distance of the charges from the polymer backbone and the less efficient electrostatic repulsion, as compared with the polymers of the lower generations. A back folding of the chains, as recently reported^{3a} for the higher generations of negatively charged dendronized polymers in dilute solution, could also explain the present findings. Furthermore it is interesting to note that the contour length of the denpols decreases^{2b} as the number of generation rises.

Figure 15 gives a more general picture of the effects of the incorporation of bulky side groups on the spatial extension of isolated coils. The very similar and extremely large $[\eta]M$ values for the first and of the second generation of the high molecular

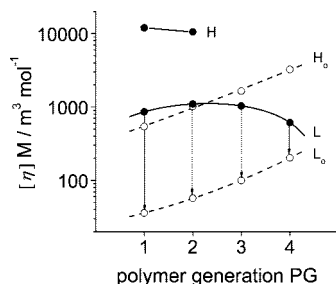


Figure 15. As Figure 14, but plotting the molar hydrodynamic volume of isolated coils on a logarithmic scale and including the data for the higher molecular weight CDPs and for the solutions of the UDPs in chloroform (open symbols). The arrows indicate how the $[\eta]M$ values for the corresponding charged and uncharged polymers interrelate.

weight CDP translate to coil diameters on the order of $0.2 \mu\text{m}$. For the generations 3 and 4, this information is inaccessible, because of the insolubility of these products. The corresponding dependence for the lower molecular weight generation has already been discussed in the context of Figure 14. In contrast to the anomalous effects observed the charged polymers, the molar volumes of the UDPs increase with the number of generations steadily as expected from the increasing bulkiness of the side groups. The enlargement is more than exponential, and the corresponding curves for the lower and higher molecular weight products run approximately parallel. Two further features become immediately obvious from Figure 15. First, the coils of 1L, the lower molecular weight product of the first generation of the CDPs, are more extended than that of the 1H₀, the higher molecular weight UDP of the first generation. This observation is clearly due to the electrostatic repulsions in the former product. The second interesting feature is visualized by the arrows drawn in Figure 15. They indicate the diminution of the differences in the chain dimensions of the corresponding lower molecular weight charged and uncharged samples upon the addition of a further generation of dendrons.

As already mentioned earlier, this phenomenon is likely due to the ability of the third and fourth generation to arrange the peripherically attached charges such that the main chain may remain as close as possible to its unperturbed extension.

5. Conclusions

The present study on the intrinsic viscosities of peripherically charged and uncharged dendronized poly(methyl methacrylate)s and their comparison with the $[\eta]$ values of a linear polyelectrolyte (Na-PSS) and with uncharged linear polymers reveals the following features: The intrinsic viscosities of solutions of CDPs in water are for all generations markedly lower than that of Na-PSS in the same solvent, despite the fact that the number of charges per monomeric unit is by a factor of 2 to 16 times larger in the former than in the latter case. The $[\eta]$ values of the UDPs in chloroform are at the same degree of polymerization comparable to that of typical linear uncharged polymers in organic solvents and vary considerably less with the numbers of generations than that of the CDPs in water. With both dendronized polymers, $[\eta]$ decreases continuously as the number of generations rises from one to four; for CDP, this effect amounts to more than 1 order of magnitude in contrast to the $[\eta]$ values of the UDPs, which are roughly half. These findings are not trivial in view of the bulky side groups and the higher charge density in case of the polyelectrolytes. Both features should give rise to an expansion of the coils rather than to their shrinkage as the number of generations rises.

The following explanations are proposed for the observations described above. The most probable one is based on the fact that the dendrons contain groups that may interact very favorably

with each other depending on the particular spatial situation. Because of the fact that the positional freedom increases from generation to generation, one can expect that the importance of favorable intramolecular interactions between -NH and -O-groups rises. This feature should affect charged and uncharged products in a similar manner. The increasing preference of intramolecular interactions at the expense of interactions with the solvent is actually testified by the fact that the high molecular weight samples of the third and of the fourth generations of the CDP are no longer soluble in water; for the corresponding lower molecular weight products, the larger entropies of mixing suffice to keep them in solution. An interpretation of the effects resting on hydrophobicity increase, which rises with the number of generations, appears very unlikely because it should cause an expansion of coils in the case of the solutions of the UDPs in chloroform, in contrast to the experimental observations, and is therefore not taken into account.

The more than exponential increase in viscosity with rising polymer concentration ($B < 0$), measured for the higher generations of both types of polymers, is consistent with the changes in the intrinsic viscosities and their interpretation. The lower $[\eta]$ values correspond to larger volume fractions of the polymer segments in the isolated coils, which means that the probability to establish intermolecular contacts between polymer segments at finite concentrations increases with the number of generations. The observed hydrodynamic effects can therefore be attributed to a larger extent of substitution of intramolecular contacts between polymer segments by intermolecular contacts, leading to the so-called pull-along effect¹² and to higher energy dissipation.

The much larger coil shrinkage from generation to generation in the case of the CDPs as compared with the UDPs requires an extra interpretation. This feature is attributed to the increasing distance of the charges from the polymer backbone. Arguing along this line is consistent with the observation that the $[\eta]$ values of the first generation products are for a given contour length of the chain already considerably lower than that of the unbranched Na-PSS. For the higher generations, the ability of the charges to evade the neighborhood of other charges is still much higher and results in a pronounced diminution of $[\eta]$. This reasoning fits well into the observation that the intrinsic viscosities of the charged and of the uncharged products approach each other as the number of generations rises. It is also consistent with the finding that the molar hydrodynamic volume of the polyelectrolyte coils $[\eta]M$ becomes maximum for the second generation. When going from the first to the second generation, the increase in the molar volume of the monomeric unit and consequently in M is larger than the decrease in $[\eta]$ caused by the larger distances of the charges from the polymer backbone. With the further addition of dendrons it is the latter effect that dominates over the increase in volume.

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