Quantitative Description of the Intrinsic Viscosity of Branched Polyelectrolytes

Markus Antonietti,* Andreas Briel, and Stephan Förster

Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Kantstrasse 55, D-14513 Teltow-Seehof, Germany

Received November 19, 1996; Revised Manuscript Received February 20, 1997⊗

ABSTRACT: A set of critically cross-linked polystyrenesulfonates with fractal geometry having molecular weights in the range $4.96 \times 10^5 < M_w < 3.07 \times 10^6$ was prepared and characterized by viscometry in salt free aqueous solutions. Also these structures show the polyelectrolyte effect, which is a strong increase in reduced viscosity with decreasing concentration. Contrary to that in linear chains, the viscosity below the overlap concentration turned out to be molecular weight independent, which interestingly bridges the behavior between spheres and linear chains. A quantitative evaluation of the data on the basis of a recently decribed model of polyelectrolyte viscosity considering single particle and cooperative multiparticle effects of the charges on viscosity reveals that the complete dependence on polymer concentration is described by assuming only the effective charge number per polymer molecule, Z_{eff}. It is not necessary to assume any concentration-dependent conformational changes.

1. Introduction

In a recent paper, we have shown that the polyelectrolyte effect, i.e. a strong increase in reduced viscosity with decreasing concentration, is also found for small spherical polyelectrolyte microgels.[1] This confirmed the earlier observations of Ise on charged colloids (see for instance ref 2) and proves that the polyelectrolyte effect is mainly due to the increase of intermolecular forces with decreasing concentration, and a rod−coil transition as the main reason as still described in many textbooks of polymer science can be excluded. In addition and due to the simplicity of the spherical model system, we were able to describe the salt as well as the concentration dependence in a quantitative fashion with a theoretical approach considering the extra influence of electrostatics via the single particle properties as well as via the cooperative coupling of all particles. This is performed via appropriate addition of a Barker−Henderson-term[3] describing the electrostatic perturbations of the single-particle Einstein-viscosity and a Hess−Klein term which considers the influence of the cooperative multiparticle coupling onto viscosity.[4] It must be underlined that this approach contains just one free parameter but still describes all quantitative and qualitative features of the whole set of data curves.

The scope of the present work is to extend the "structural parameter" (the approach of learning about polyelectrolyte behavior by variation of the molecular architecture) used in the previous work and to examine other polyelectrolyte topologies which reveal new possibilities of testing the theoretical description. In particular, branched polyelectrolytes with critical branching topology are expected to represent a unique intermediate between linear chains and spheres. It is peculiar to the new description that these structures exhibit a molecular weight independent reduced viscosity. In this context, it must be recapitulated that the reduced viscosity is strongly increasing with molecular weight for linear polyelectrolytes, where it is decreasing with size for PE-spheres (note that this is only true for polyelectrolyte spheres, whereas uncharged spheres show a molecular weight independent intrinsic viscosity).

For those reasons, we examine the solution viscosity of these polyelectrolytes and their dependence on molecular weight and concentration and apply our new theoretical approach for the solution viscosity of polyelectrolytes to the data sets.

2. Theory

The theory for the description of the solution viscosity of polyelectrolytes was described in detail in the earlier publication[1] and is just briefly recapitulated.

The reduced viscosity of a dilute polymer solution is classically described by the Huggins equation[5]:

$$\eta_{red} = [\eta]_0 + k_H[\eta]_0{}^2 c_P \tag{1}$$

Here, $[\eta]_0$ is the intrinsic viscosity, measuring the volume being hydrodynamically controlled per gram of polymer. k_H is the Huggins constant, describing the importance of binary hydrodynamic events, and it usually depends on polymer architecture and molecular weight. If the molecular weight M_P of the polymer is known, the intrinsic viscosity can be transferred into a viscosimetric effective radius R_h[5]:

$$[\eta]_0 = \frac{10}{3}\pi N_A \frac{1}{M_P} R_\eta{}^3 \tag{2}$$

N_A is the Avogadro constant. This description does not consider the influences of charges and essentially follows the hydrodynamic approach of the reduced viscosity first given by Einstein.

The presence of charges alters the single particle hydrodynamics. This is due to the fact that a counterion cloud extends into the solution but is coupled to the polymer backbone and is therefore hydrodynamically active. As a perturbation correction to the Einstein case, an effective radius may be introduced. In the perturbation theory by Barker and Hendersen,[3] the effective hard sphere diameter is chosen such that

$$R_{el} = R_\eta + \int_{R_0}^{r'} \left(1 - \exp\left[-\frac{\phi}{kT}\right]\right) dr \tag{3}$$

where r' is the distance where the electrostatic potential ϕ has decayed to zero. Inserting the standard screened

---

⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1997.

S0024-9297(96)01702-0 CCC: $14.00

electrostatic potential, Russel et al.[6] obtained for R_{el}

$$R_{el} = \frac{1}{2\kappa}\ln(\alpha/\ln(\alpha/\ln(\alpha/\ln(\alpha/...)))) \tag{4}$$

with

$$\alpha = Z_{eff}^{\;2} l_B \kappa \frac{\exp[2\kappa R]}{(1+\kappa R)^2} \tag{5}$$

κ is the Debye–Hückel constant, and l_B is the so-called Bjerrum length (the length where electrostatic energy and thermal energy balance) given by

$$l_B = \frac{e^2}{4\pi\epsilon\epsilon_0 kT} \tag{6}$$

$$\kappa^2 = 4\pi l_B N_L \sum_i Z_i^{\,2} c_i' \tag{7}$$

Here, ϵ is the dielectric constant, and c_i' and Z_i are the molar concentrations and effective charge numbers of all ionic species i, respectively.

At high ionic strength where electrostatic interactions are effectively screened, $R_{el} \rightarrow R_0$.

A question is how to handle such a perturbation correction in the limit of low and intermediate ionic strengths where electrostatic interactions are important. A possible consistent description, which is motivated by the experimental results, is to postulate an overall radius R_{tot} which is hydrodynamically not accessible for other particles in a manner such that

$$R_{tot} = R_0 + R_{el} = R_0 + {}^1/_2 Z_{eff}^{\;2} l_B \tag{8}$$

Z_{eff} is the effective charge number per polymer which is discussed in more detail below. Equation 8 may be visualized as the buildup of a "Bjerrum shell" of thickness $R_B = Z_{eff}^2 l_B/2$, much like the buildup of a double layer or Stern layer. With decreasing ionic strength the effective radius of a particle increases, since the effective charge Z_{eff} increases with decreasing ionic strength. At high ionic strength where electrostatic interactions are effectively screened, $Z_{eff} \rightarrow 0$.

The meaning of Z_{eff} plays an imporant role in all following discussions. Z_{eff} is the effective charge number per particle which is obtained by rescaling the complicated multiion–ion interactions to a screened Coulomb potential. Since there is—to our knowledge—no simple way to calculate Z_{eff} for a charged extended object in the presence of low molecular weight ions, Z_{eff} is used as a fit parameter, only.

In addition to the influence of charges on the single particle hydrodynamics of an polyelectrolyte, one has also to consider a cooperative coupling of all particles, which also severely influences the reduced viscosity. This contribution describes the restriction of the mobility of one particle in the electric field of all the others and was first calculated by Hess and Klein[4] as:

$$\eta_{red} = \frac{1}{160}\left(\frac{4\pi l_B N_L}{M_w}\right)^{1/2} r_H \frac{Z_{eff}^{\;4} c_p}{\left(\frac{2M_s^{\;2}}{M_p} c_s' + Z c_p\right)^{3/2}} \tag{9}$$

Here, we employ a version which was rewritten in terms of the specific notations of polymer analysis.[6] M_s is the molecular weight of a low molecular weight salt which might be present in solution.

To describe experimental results, the contributions from stresses resulting from hydrodynamics (including the effect of the counterion cloud on hydrodynamics) and electrostatic coupling may simply be summed up as suggested by eq.[10] This crude approximation neglects possible cross-terms within the underlying Green–Kubo formalism, but is—to the best of our knowledge—the only approach available. As the final equation which is used to describe the experimental data, we obtain

$$\eta_{red} = [\eta]_0 + k_H[\eta]_0^{\;2} c_p + \frac{1}{160} r_H \left(\frac{4\pi e^2 N_L}{M_P \cdot \epsilon\epsilon_0 kT}\right)^{1/2} \frac{Z_{eff}^{\;4} c_p}{\left(2\frac{M_P}{M_S} c_s + Z_{eff} c_p\right)^{3/2}} \tag{10}$$

with

$$[\eta]0 = \frac{10}{3}\pi N_A \frac{1}{M_P}(R_\eta + R_B)^3 \qquad r_H = R_\eta + R_B \tag{11}$$

Equation 11 splits the viscometric active size of the polyelectrolyte molecules in the viscometric radius R_h of the hypothetically uncharged structure and the additional Bjerrum radius R_B. Since R_B is also related to Z_{eff} via eq 8, this equation posesses only two fitting parameters, R_B and k_H, where k_H can be additionally fixed to be on the order of the usual values for the molecular architecture examined.

The numerical evaluation of this formula results in the prediction of three different regimes of the viscosity behavior:

(a) The theory describes a first regime at very low concentrations $c < c^{**}$ where the particles start to "feel" the electric field of each other which results in an increased intermolecular coupling of the polyelectrolytes. The viscosity is however controlled by single-particle properties. For simplicity, c^{**} can be attributed to the maximum in the reduced viscosity. It is expected that the reduced viscosity in this region is described by the particle extension plus "Bjerrum shell", where the size of the particles can usually be neglected; i.e., we expect in this region structural parameters to be insignificant. The onset of intermolecular coupling can be approximated by a linear expansion of the Hess–Klein term and results in a very high apparent k_H parameter.

(b) In an intermediate concentration regime $c^{**} < c < c^*$, the viscosity is governed by the intermolecular coupling between the polyelectrolytes which is described within the framework of the Hess–Klein description. In this range, an additive single-particle contribution (single-particle hydrodynamics including a "Bjerrum-shell") is required to describe both the magnitude and the concentration scaling of the reduced viscosity.

(c) At concentrations $c^* < c$, the hydrodynamic equivalent spheres start to overlap, the electrostatic interactions are largely screened, and binary or cooperative hydrodynamic events become important. The onset of this behavior is considered by the Huggins expansion. For simplicity, c^* can be attributed to the expected minimum of the reduced viscosity.

3. Experimental Section

3.1. Polymer Synthesis. The synthesis of the critically cross-linked polystyrene precursors with fractal structure characterstics as well their characterization was already described in ref 8. This route essentially followed the experi-

Table 1. Polymeranalytical Data of the Sulfonated Critically Cross-Linked Microgels, As Calculated from the Data of the Parental Systems[a]

sample	M_w/g mol^{-1} [b]	M_w/M_n	$[\eta]_p$[c]/L g^{-1}
SMPE/F5	3.07×10^6	2.12	0.090
SMPE/F6	8.16×10^5	1.80	0.052
SMPE/F7	4.96×10^5	2.56	0.044

[a] M_w is the weight average of molecular weight, and M_w/M_n, the polydispersity index. For comparison, also the intrinsic viscosities of the uncharged polymer, $[\eta]_p$, are added. Note that the degree of sulfonation is always ca. 70%, which is adjusted by synthesis. [b] Calculated from parental hyperbranched microgels. [c] Taken from parental microgels.

ments described by Staudinger in the 1930s who made the first polymeric fractals, but did not call them that.[9] From this sample set, we selected a number of fractions, the molecular characteristics of which are summarized in Table 1.

Sulfonation of these critically cross-linked polymers was performed either with H_2SO_4/P_2O_5 according to the Vink procedure[10] or with a synthesis using H_2SO_4/Ac_2O in 1,2-dichloroethane,[11,12] thus resulting in polystyrenesulfonates with a degree of sulfonation of about 95% or 70%, respectively. Model reactions with narrowly distributed polystyrene standards which are characterized after sulfonation by aqueous GPC showed essentially the absence of chain scission or cross-linking reactions.[13] Since both degrees of sulfonation show for cross-linked polymers a very similar behavior, only data for the samples with 70% are presented. This is due to the fact that this synthesis is a salt-free synthesis, and the samples are more easily purified.

The polyelectrolytes were dialyzed against Millipore water and stored as 1 wt % stock solutions over a carefully purified, mixed-bead ion exchange resin in water.

3.2. Viscometric Measurements. All viscosity measurements were performed in water at 25.0 °C using an automatic Schott AVS360 instrument (Ubbelohde viscometers), which allows a reproduction of the flow times with an accuracy of 0.03 s. The solutions were made by diluting the stock solutions in bidistilled, deionized water. The flow times were taken by measuring subsequent dilutions, and each flow time was reproduced five times. The dilution and the measurements were stopped when the viscosity difference between the polyelectrolyte solution and pure water drops below 10%. It must be underlined that all measurements are performed with the polystyrenesulfonic acids, i.e. with the proton as the counterions, since our earlier experiments showed that the protons produced the highest viscosity effects.[1] This is important, since only the polyacids allowed the extension of the measuring range toward the presented small concentrations as well as a suppression of the influence of the autoprotolysis of water.

4. Results and Discussion

Parts a and b of Figures 1 already show the reduced viscosity for the set of samples SMPE/F5−F7 as a function of polyelectrolyte concentration (g/L) in an aqueous salt-free solution in two different representations on a linear (a) and a logarithmic scale (b) versus log c_P.

Obviously, the polyelectrolyte effect is also present for solutions of the critically cross-linked polyelectrolytes. The reduced viscosity of salt-free solutions is increasing with decreasing polyelectrolyte solution. For the smallest concentrations, the reduced viscosity reaches values as large as 0.66 L/g, a value which is at least 1 order of magnitude higher than the corresponding values of the uncharged polystyrene microgels under good solvent conditions.[8] Probably due to the restricted concentration range (which is limited by our conservative decision to stop dilution when the viscosity difference to the pure solvent drops below 10%), no maximum of the reduced viscosity is observed. As shown many times in the literature for linear polyelectrolytes,[14−18] a maximum occurs when the effective ion concentration due to the polymer is of the order of the concentration due to low molecular weight salt. Assuming autoprotolysis of water, only, this is below the range of our experiments.

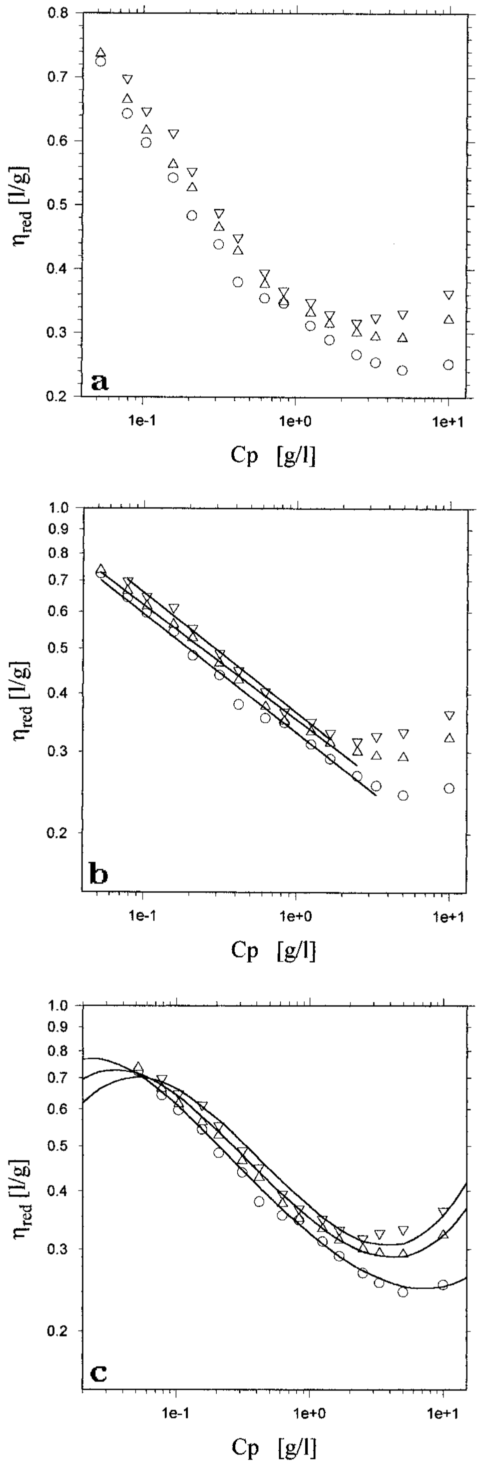

Figure 1. Concentration dependence of the reduced viscosity of critically cross-linked fractal polyelectrolytes with different molecular weights: (▽) SMPE/F5; (△) SMPE/F6; (○) SMPE/F7. The same data are presented in a semilogarithmic (a) as well as in a double-logarithmic plot (b). The straight line in plot b represents a fit with a scaling law $\eta_{red} \sim c_P^{-0.25}$. Part c shows the fit of the data according to eqs 10 and 11 and the fit parameters listed in Table 2. The fit function is shown in a wider range to allow estimating of some trends.

Interestingly enough and best seen in the double-logarithmic presentation, the concentration dependenc-

Table 2. Fit Parameters Used for the Quantitative Description of the Viscosity Data According to Eq 10[a]

sample	$Z_{\rm eff}$	$k_{\rm H}$	$[\eta]_0$/L g^{-1}
SMPE/F5	9.8	0.9	0.182
SMPE/F6	8.9	0.6	0.143
SMPE/F7	8-3	0.2	0.139

[a] $Z_{\rm eff}$ is the effective charge number per particle; $k_{\rm H}$ is the Huggins constant. $[\eta]_{\rm el}$ is the single particle excluded volume as calculated by the model of a Bjerrum shell.

es of the reduced specific viscosity can be described by a scaling law being valid for all particle sizes, given by

$$\eta_{\rm red} \sim c_{\rm P}^{-0.25\pm0.01} \tag{12}$$

This is the same scaling law being found during examination of the spherical model polyelectrolytes,[1] which was explained by summing up the Bjerrum sphere and the Hess−Klein contribution.

Using this approach and eqs 10 and 11, we are able to fit all curves with just two parameters. The quality of the fit is shown in Figure 1c and is—considering the low number of free parameters—rather good. Since the fits predict a maximum of the reduced viscosity slightly below the accessible concentration range, the fit curves are continued in this concentration range.

The corresponding fit parameters $Z_{\rm eff}$ and $k_{\rm H}$ are summarized in Table 2.

Since $[\eta]_0$ is directly related to $Z_{\rm eff}$, we can also express our fit in terms of the single particle property $[\eta]_0$ (including the Barker−Henderson-type influence of electrostatics on the excluded volume). The resulting data for the three molecular weights are also presented in Table 2. In all cases, $[\eta]_0$ adds a major contribution to the reduced viscosities which is on the order of the viscosity increase due to the cooperative electrostatic coupling. The molecular weight dependence of $[\eta]_0$ is low. A comparison with the intrinsic viscosities of the uncharged parental critically cross-linked microgels reveals that the Bjerrum shell makes up about 50−80% of the single particle hydrodynamic volume.

Surprisingly at a first glance, we find only a very weak molecular weight dependence of the reduced viscosity at concentrations below a critical overlap concentration, which is for SMPE/F5 on the order of 2.5 g/L. Looking at eq. 9, this insensitivity against molecular weight for fractals is easy to understand and even predicted by theory. For the limit of low salt concentrations $c_{\rm P}/c_{\rm S} \gg 1$ we can simplify:

$$\eta_{\rm red} \sim \frac{R_{\rm H}}{M_{\rm w}^{0.5}} Z_{\rm eff}^{5/2} \tag{13}$$

Assuming good solvent conditions, we know from the uncharged parental microgels that $R_{\rm H} \sim M_{\rm w}^{0.47}$;[9] i.e. all intrinsic molecular weight dependences balance, and we expect the viscosity to depend on the effective charge number, only. For linear polymer chains, a $Z_{\rm eff}$ independent of the molecular weight was reported,[1] and the fit parameter listed in Table 2 shows within the numerical stability about the same trend. This means that the found molecular weight independence underlines the applicability of the Hess−Klein description for the intermolecular contributions to the reduced viscosity, since no theory working only with molecular parameters (such as hyd0dynamic size) can explain such a behavior.

The difference in molecular weight between the three fractions and the different hydrodynamic size becomes visible at higher concentrations when the electrostatic interactions are screened and binary hydrodynamic events become important. This overlap concentration c^* is for simplicity assigned to the minima in the reduced viscosity curves, which indeed show a pronounced molecular weight dependence and goes from 2.5 g/L for SMPE/F5 to 4 (SMPE/F6) and 7g/L (SMPE/F7). This is about the molecular weight dependence we expect from the reduced viscosities of the uncharged parental fractal microgels.

At the end of the discussion we might again comment on the observed low value of the effective charge, which is on the order of 8−10 and therefore very similar to the value found for linear chains. It must be repeated that the effective charge in our viscosity measurements characterizes interparticle electrostatic interactions, i.e., the potential energy that one particle experiences in the mean electric field produced by its neighboring particles. Here it is important that local electroneutrality requires most of the counterions to be distributed inside the particle (at $R < R_0$) or near the particle obeying the Poisson−Boltzmann distribution. Conceptually, we may define a distance R' at given salt concentration which is the minimal distance being explored by other colloidal particles and where the major part of the counterion cloud may be located within. The force field of the resulting charge distribution, including dipoles or higher multipoles, either permanent or induced by electrokinetic effects, is approximated with an equivalent point charge with a Debye−Hückel potential, which may indeed be very low.

5. Conclusion and Outlook

It was shown that critically cross-linked fractal polyelectrolytes show a strong polyelectrolyte effect in the solution viscosity experiment. It was possible to describe the concentration dependence in an intermediate concentration regime with a $\eta_{\rm red} \sim c_{\rm P}^{-0.25}$ law, which is similar to the intermediate scaling of spherical polyelectrolytes. We were able to describe the concentration dependence in a quantitative way by a theory which combines the Hess−Klein and the Barker−Henderson formalisms, having as the only adjustable parameter the effective charge number $Z_{\rm eff}$. Since $Z_{\rm eff}$ is approximately molecular weight independent and all intrinsic molecular weight dependences balance within the Hess−Klein equation for the critical Staudinger microgels, we even expect a molecular weight independent reduced viscosity which indeed is found in an intermediate concentration regime. The experimental verification of this independence, a peculiar prediction of eq. 10, supports the applied theoretical model strongly.

Slightly below the accessible concentration range, this theory predicts a maximum also for branched polyelectrolytes, the determination of which would improve significantly the accuracy of the effective charge number and the remaining molecular weight dependence. To extend the range of measurements, new techniques of precise viscosity determination will have to be developed, which will allow a still more detailed look into the theoretical description of polyelectrolyte behavior.

Acknowledgment. Financial support by the Otto-Röhm-Gedächtnisstiftung, the Fonds der chemischen Industrie, and the Max Planck Society is gratefully acknowledged.

References and Notes

(1) Antonietti, M.; Briel, A.; Förster, S. *J. Chem. Phys.* **1996**, *105*, 7795.
(2) Yamanaka, J.; Matsuoka, H.; Kitano, H.; Ise, N. *J. Colloid Interface Sci.* **1990**, *134*, 92.
(3) Barker, J. A.; Henderson, D. *Annu. Rev. Phys. Chem.* **1972**, *23*, 439.
(4) Hess, W.; Klein, R. *Adv. Phys.* **1983**, *32*, 173.
(5) Flory, J. P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(6) Russell, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: Cambridge, England, 1989.
(7) Antonietti, M.; Förster, S.; Zisenis, M; Conrad, J. *Macromolecules* **1995**, *28*, 2270.
(8) Antonietti, M.; Rosenauer, C. *Macromolecules* **1991**, *24*, 3434.
(9) Staudinger, H.; Husemann, E. *Chem. Ber.* **1935**, *68*, 1618.
(10) Vink, H. *Makromol. Chem.* **1970**, *131*, 133.
(11) Thaler, W. A. *Macromolecules* **1983**, *16*, 623.
(12) Orler, E. B.; Yontz, D. J.; Moore, R. B. *Macromolecules* **1993**, *26*, 5157.
(13) Briel, A. Diploma thesis, Marburg, 1993.
(14) Cohen, J.; Priel, Z.; Rabin, Y. *J. Chem. Phys.* **1988**, *88*, 7111.
(15) Cohen, J.; Priel, Z. *Macromolecules* **1989**, *22*, 2356.
(16) Cohen, J.; Priel, Z. *J. Chem. Phys.* **1990**, *93*, 9062.
(17) Vink, H. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 801.
(18) Förster, S.; Schmidt, M. *Adv. Polym. Sci.* **1995**, *120*, 53.

MA9617025