Model Mono-, Di-, and Tri-ω-Functionalized Three-Arm Star Polybutadienes. Synthesis and Association in Dilute Solutions by Membrane Osmometry and Static Light Scattering

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ABSTRACT: Three-arm polybutadienes with one, two, and three functional end groups were prepared by anionic polymerization using [3-(dimethylamino)propyl]lithium and *sec*-butyllithium as initiators and methyltrichlorosilane as linking agent. Characterization carried out on the dimethylamine-capped polymers by size exclusion chromatography (SEC), in THF, low-angle laser light scattering (LALLS) in THF, and membrane osmometry (MO) in toluene indicates a high degree of molecular and structural homogeneity. The 1,2 content, determined by NMR spectroscopy, of the arms having the functional groups was higher (12–32%) than that of the arms without the functional groups (7–10%), owing to the tertiary amine group of the initiator. The dimethylamine end groups were transformed to the highly polar sulfozwitterionic ones by reaction with cyclopropanesultone. Association of the different ω-functionalized star polybutadienes was studied in dilute solutions of cyclohexane by MO and LALLS. It was found that although the dimethylamine-capped polybutadienes do not associate, the corresponding zwitterionic species associate strongly in this solvent. At fixed molecular weight of the arms, the degree of association increases with decreasing number of functional groups and, for the same number of functional groups, with decreasing molecular weight of the arms. The trifunctional species form gels at concentrations needed for MO experiments. Comparison with linear ω-zwitterionic polybutadienes in cyclohexane shows that the stars associate less strongly, maybe due to the sterically hindered star structure (monofunctional species) and to intramolecular interactions (di- and trifunctional species).

Introduction

Over the last decade considerable interest has developed in polymers bearing polar groups at different positions on the macromolecular chain.[1–8] The introduction of these groups produces dramatic changes in the properties of the parent polymers. For this reason these functionalized polymers not only are of theoretical interest[9–13] but have also found commercial applications.[14,15]

Macromolecules with functional polar groups located at specific sites of the chain provide the simplest system for the study of the influence of these groups on the properties of the precursor polymer.[16–20] The modification of the properties is caused by the association of the polar groups in a nonpolar environment.

Fetters and co-workers[21–24] studied dilute-solution and melt properties of linear polyisoprenes having at the chain end the weakly polar dimethylamino or the strongly polar sulfozwitterionic group. They also investigated star polyisoprenes with two, three, and twelve arms (one sample for every kind of star), having the same functional group at the end of each arm. They found that very strong associations exist in cyclohexane for linear samples with the zwitterion groups whereas for amine-functionalized polymers the association was rather weak. Star polymers were not extensively studied, but those with the sulfozwitterion groups were found to form gels that could be dissolved by the addition of small amounts of the polar compound 1-heptanol.

Recently, Pispas and Hadjichristidis[25,26] extended this work to block copolymers of styrene and isoprene having the same polar groups at one, the other, or both ends. The degrees of association are lower than those of the corresponding linear polyisoprenes probably because of the high polarizability of the phenyl rings. Diffusion and viscometric data strongly support the star shape of the aggregates.

In a series of papers Kennedy and co-workers[27–32] reported the synthesis and the mechanical properties of three-arm star polyisobutylenes with metal sulfonate end groups. The data suggest the existence of a relatively strong network, which contains in addition to the thermoreversible, covalent cross-links coming from the star structure.

Storey and co-workers[33] prepared three-arm star hydrogenated polybutadienes with oligomeric sulfonated polystyrene tails. These samples provide poor mechanical properties, meaning that the networks formed are weak. A high incidence of looping, i.e., the situation in which two or three arms of the same molecule are incorporated into the same multiplet, is proposed by the authors.

In this paper we present the synthesis, characterization, and dilute-solution properties of three-arm star polybutadienes having one, two, and three functional (dimethylamine and zwitterion) end groups (Chart 1). The synthetic procedure was similar to the one used by Pennisi and Fetters[34] for the preparation of asymmetric polystyrene three-arm stars and by Hadjichristidis et al. for the synthesis of 3-miktoarm star copolymers of the A_2B type.[35] The association behavior of these polymers in the nonpolar solvent cyclohexane was studied by low-angle laser light scattering (LALLS) and membrane osmometry (MO).

Experimental Section

The polymer synthesis was performed in vacuo in all-glass reactors with breakseals and constrictions. The solvent (benzene), monomers (butadiene, styrene, and 1,1-diphenylethylene), linking agent (methyltrichlorosilane), and terminating agent (methanol) were purified using well-established vacuum line methods.[36,37] *sec*-Butyllithium (*sec*-BuLi) and

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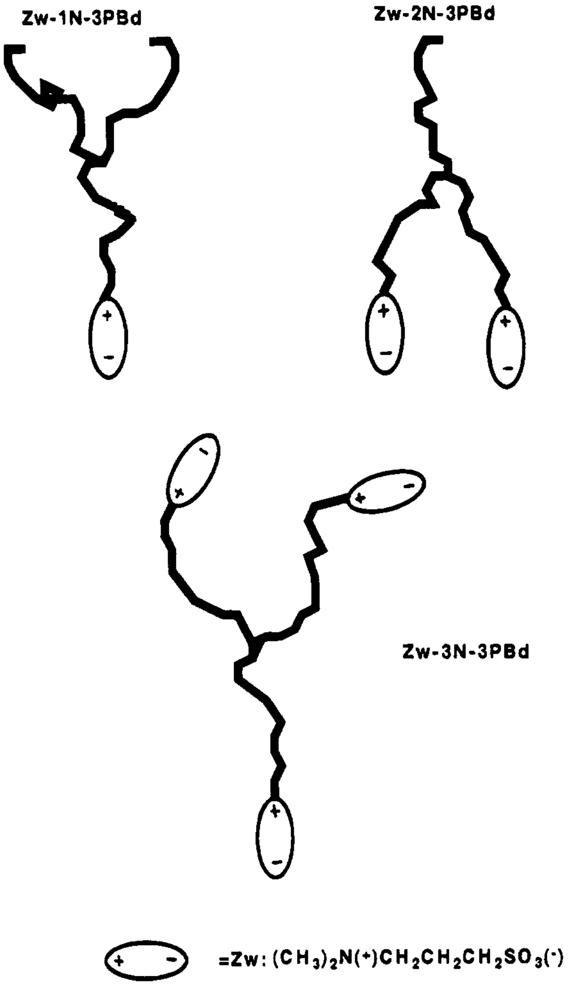
Chart 1



[3-(dimethylamino)propyl]lithium (DMAPLi), prepared from the corresponding chloride and lithium dispersion, were used as the initiators for the polymerizations. Details about the synthesis and analysis of DMAPLi will appear in a forthcoming paper.[38]

Dimethylamine-capped star polymers were fractionated by addition of methanol to a ca. 1% w/v polymer solution in toluene. The polymers were precipitated in excess methanol, dried under vacuum, and stored in a vacuum oven.

The amine polymers were converted to the sulfozwitterionic ones by reaction of the dimethylamine groups with excess cyclopropanesultone (amine/sultone ca. 1/10). A dilute solution (ca. 2% w/v) of the amine precursor in THF was reacted with the sultone under argon for several days at 70 °C. The solvent was evaporated almost to dryness, and the zwitterion-capped polymer was precipitated in acetone and washed several times to remove excess sultone.

SEC experiments were accomplished at 30 °C using a modular instrument consisting of a Waters Model 510 pump, a Waters Model U6K sample injector, a Waters Model 401 differential refractometer, and a set of four μ-Styragel columns with a continuous porosity range from 10^6 to 10^3 Å. The columns were housed in an oven thermostated at 30 °C. The flow rate was 1 mL/min and the carrier solvents were THF and chloroform.

A Wescan Model 231 membrane osmometer at 37 °C was used for the determination of the number-average molecular weight M_n and second virial coefficient A_2. Toluene and cyclohexane distilled over CaH_2 were the solvents. RC-51 membranes were used in all cases. The M_n values were obtained from the corresponding $(\pi/c)^{1/2}$ vs c plots, where π is the osmotic pressure and c the concentration.

The weight-average molecular weight M_w and second virial coefficient A_2 were measured with a Chromatix KMX-6 low-angle laser light scattering photometer at 25 °C for $\lambda = 633$ nm. THF refluxed over sodium and cyclohexane refluxed over CaH_2 were distilled just prior to use. Trifunctional zwitterion-capped stars form gels in cyclohexane even at low concentrations. All the solutions were clarified by filtration through 0.22 μm pore size Nylon filters. For the zwitterion-capped samples fluctuations of the scattered light intensity were relatively large. The M_w and A_2 values were obtained from plots of $(Kc/\Delta R_\theta)^{1/2}$ vs c, where K is a combination of known optical constants and ΔR_θ is the excess Rayleigh ratio.

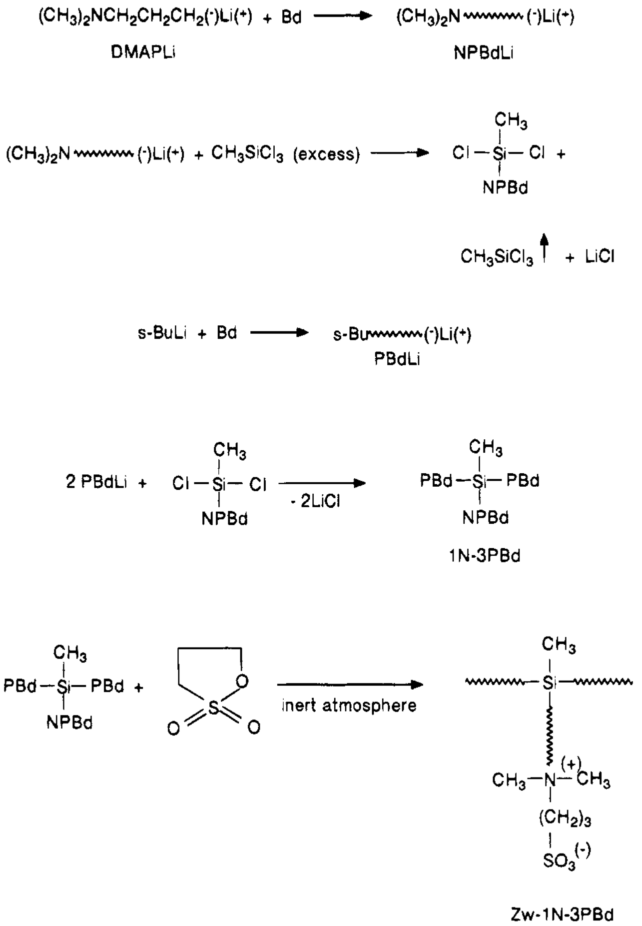


Figure 1. Basic reactions for the synthesis of the 1N-3PBd and Zw-1N-3PBd stars.

Refractive index increments, dn/dc, at 25 °C were measured with a Chromatix KMX-16 refractometer operating at 633 nm and calibrated with NaCl solutions. The dn/dc values are in excellent agreement with values published in the literature for polybutadiene in THF and cyclohexane.[39] For THF solutions the values are between 0.130 and 0.133 mL/g and for cyclohexane solutions between 0.105 and 0.110 mL/g depending on the microstructure of the samples.

The microstructure of the polybutadiene stars was obtained by ^{1}H-NMR and ^{13}C-NMR spectroscopy (Bruker AC200) at 30 °C in $CDCl_3$.[40]

Results and Discussion

Three series of polymers were prepared with one, two, and three functional end groups. The designation used for these samples gives information about the number of functional groups (1, 2, or 3) and the type of functional group (N for the amine-capped and Zw for the zwitterion-capped samples). The number following differentiates the samples of the same series. For example the sample 1N-3PBd15 is a three-arm polybutadiene star with one dimethylamine end group. Zw-1N-3PBd15 is the corresponding zwitterion-capped polymer (see also Chart 1).

In Figure 1 a schematic representation of the sequence of reactions used for the synthesis of 1N-3PBd and Zw-1N-3PBd samples is shown. In the first step a

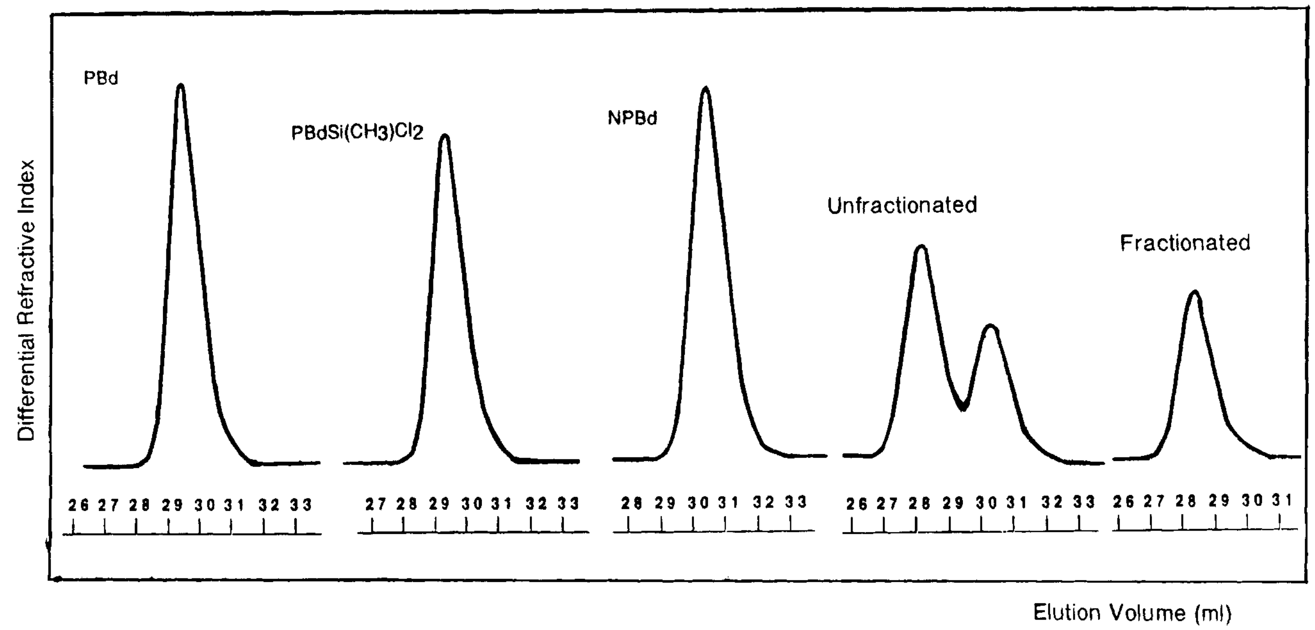


Figure 2. SEC chromatograms concerning the synthesis of the 2N-3PBd40 star polymer.

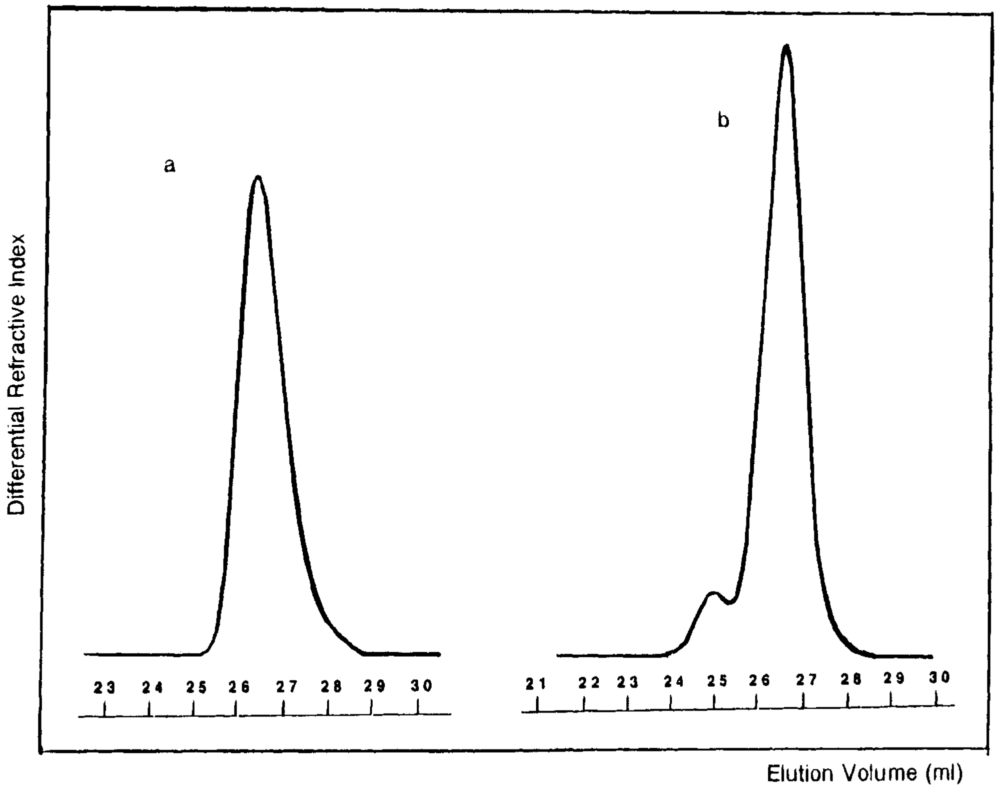


Figure 3. SEC chromatograms of (a) linear PBd (M_n = 8200, by SEC) with 3–4 units of styrene and (b) chlorosilane-capped arm.

solution of the living N-functionalized polybutadiene arm in benzene was prepared, with DMAPLi as the initiator. This solution was added to a large excess of methyltrichlorosilane (Si–Cl/C–Li $\simeq$ 100/1) in order to prepare the methyldichlorosilane-capped PBd. Excess methyltrichlorosilane and benzene were removed under vacuum line conditions. The polymer was repeatedly redissolved and pumped to extract traces of the silane from the bulk polymer. Finally, purified benzene was introduced into the reactor to dissolve the ω-methyldichlorosilane PBd arm.

In the second step an excess of the unfunctionalized arm, prepared by using *sec*-BuLi as initiator, was reacted with the silane-capped arm. The linking reaction was conducted at room temperature for at least 15 days. Finally, degassed methanol was added to terminate residual active anions.

A similar procedure was followed for the synthesis of 2N-3PBd stars, starting first from the reaction of the living unfunctionalized arm with excess of methyltrichlorosilane followed, after removal of excess silane, by reaction of the unfunctionalized chlorosilane-capped arm with an excess of the functionalized living arm. As an example, the synthesis of the 2N-3PBd40, as monitored by SEC, is given in Figure 2.

In the case of the samples with low arm molecular weight, a slightly different procedure was followed. When living polybutadiene B($^-$) with molecular weight

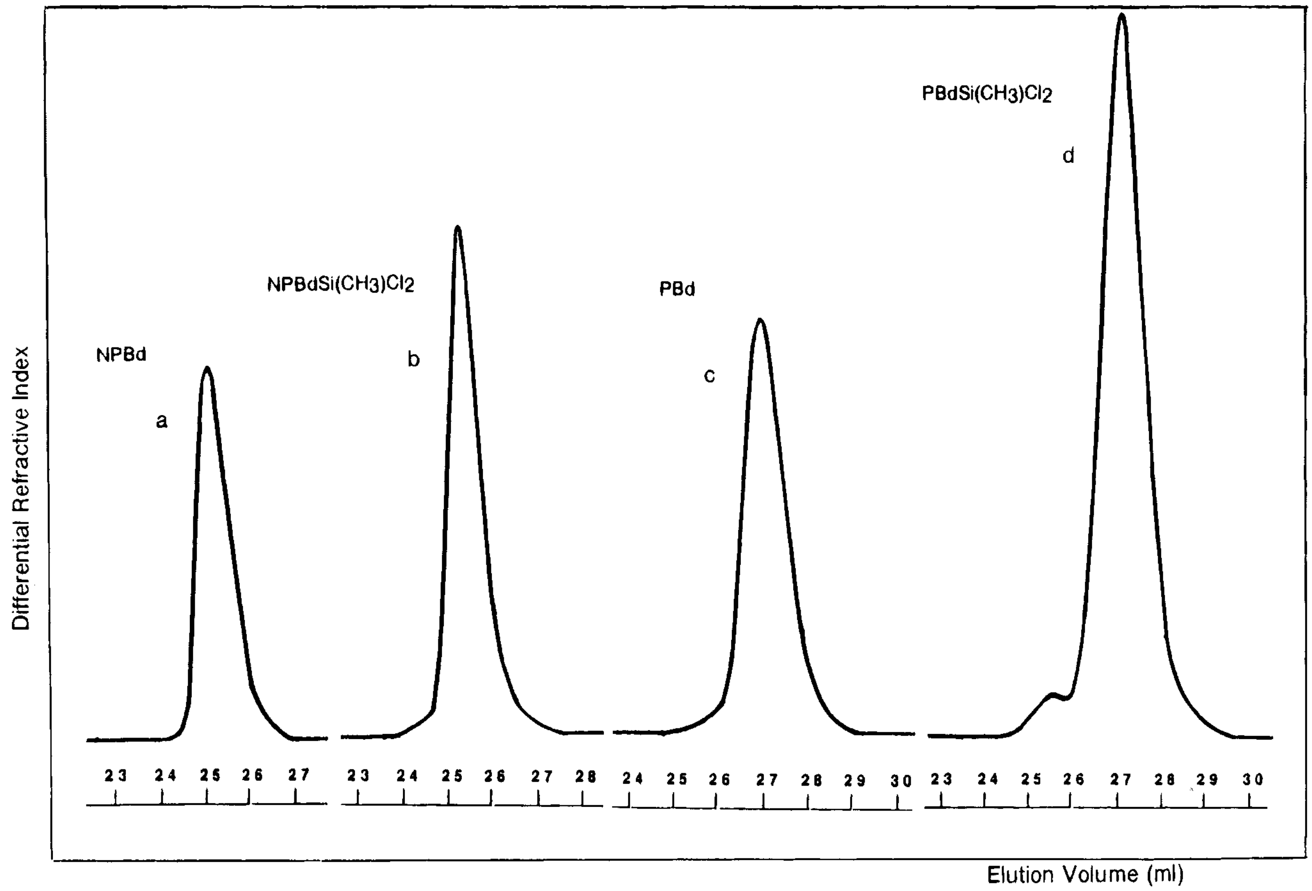


Figure 4. SEC chromatograms from the synthesis of 1N-3PBd8 (a, b) and 2N-3PBd8 (c, d): (a) NPBd arm with one unit of DPE; (b) chlorosilane-capped NPBd arm; (c) PBd arm with one unit of DPE; (d) chlorosilane-capped PBd arm.

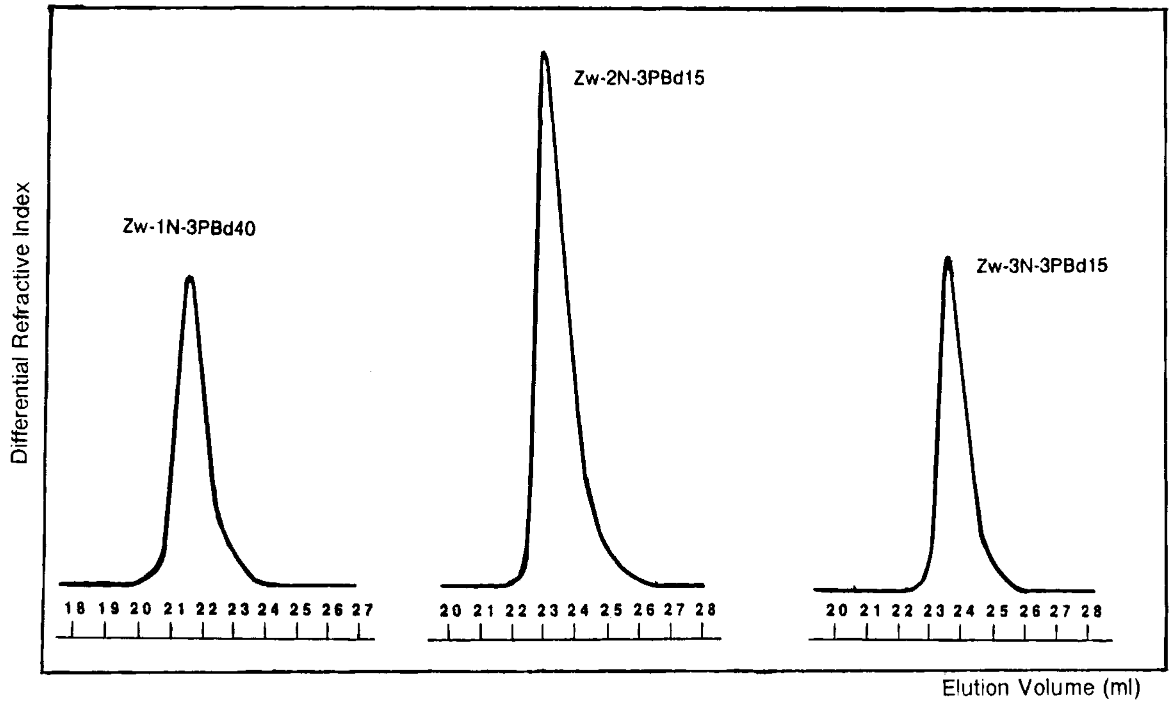


Figure 5. Representative SEC chromatograms of zwitterion-capped stars in $CHCl_3$.

below 10^4 reacts with an excess of methyltrichlorosilane, it is not possible to control the reaction to form only methyldichlorosilane-capped polybutadiene $BSi(CH_3)Cl_2$. A large amount (>10%) of the coupled product $B_2Si(CH_3)Cl$ is also formed. Subsequent reaction with the living polybutadiene $A^{(-)}$ produces a mixture of the desired A_2B and the undesired AB_2 stars. If the difference between the molecular weights of the arms A and B is very large, then it is possible to separate the A_2B and AB_2 stars by fractionation. In the present case, the molecular weights of the functionalized and the unfunctionalized arms are almost the same so that it is impossible to separate the byproduct from the desired star.

In order to minimize the coupling reaction, the living polybutadiene arm $B^{(-)}$ was capped with 3–4 styrene

Table 1. Microstructure of NPBd with Different Molecular Weights

M_n	% cis 1,4	% trans 1,4	% 1,2
5400	27.1	40.9	32.0
12600	29.2	44.8	26.0
13100	29.0	44.0	27.0
34900	33.8	47.1	19.1
35600	36.5	51.2	12.3

units. The increased steric hindrance of the living end is expected to suppress the coupling reaction. A few drops of THF were added to accelerate the crossover reaction from the butadienyllithium to the styryllithium living end. The reaction of the styrene-capped polybutadienyllithium with excess methyltrichlorosilane produced ca. 7% of the undesired product. Although the steric hindrance of the living end was increased, the result was not satisfactory because THF breaks up the association of the living ends, making them more reactive. Figure 3 reports the SEC results obtained by this procedure. This difficulty was overcome using 1,1-diphenylethylene (DPE) instead of styrene. THF was also used to transform the butadienyllithium to (diphenylethenyl)lithium living ends. The reaction of the DPE-capped living arm with the excess of silane was sufficiently efficient. The byproduct yield reached ca. 3.5% for the 2N-3PBd8 and ca. 1% for the 1N-3PBd8. The increased reactivity of the living ends due to the THF is overbalanced by the increased steric hindrance of the DPE moiety compared with styrene. Size exclusion chromatograms concerning this reaction for the synthesis of 2N-3PBd8 and 1N-3PBd8 samples are presented in Figure 4.

For the preparation of 3N-3PBd samples, DMAPLi was used as the initiator according to well-described procedures for the synthesis of symmetric homostars.[41,42]

After the sultone reaction SEC chromatograms were recorded for the zwitterion-capped stars using $CHCl_3$ as the carrier solvent. Experience with linear polyisoprenes[22] and block copolymers of styrene and isoprene[25] bearing the same polar groups has shown that adsorption on the columns occurs when THF is the carrier solvent. The polarity of the $CHCl_3$ and its tendency to be preferentially adsorbed, instead of polymers with the polar groups, suppress these effects. The SEC chromatograms in $CHCl_3$ were almost identical with those of the amine polymers in THF. Representative examples are given in Figure 5.

The tertiary amine group of the initiator is polar enough to change the microstructure of linear polybutadienes, leading to increased 1,2 content. Similar results were found for the polymerization of isoprene with DMAPLi as initiator.[21,25] The lower the molecular weight, the higher the 1,2 content, due to the increased concentrations of initiator needed for the synthesis of these samples.[43] Results from the determination of the microstructure for linear end-functionalized polymers are given in Table 1. It is clear that the 1,2 content is higher than in the conventional polymer (7–10%) and varies from 12 to 32%.

The molecular characteristics of the amine-capped polymers in toluene and THF have been collected in Table 2. The functionality f of the stars, calculated from the M_n of the star and the average M_n of the arms in all cases, is close to 3. The polydispersity index M_w/M_n, calculated from M_w(LALLS) and M_n(MO), is low and in agreement with the one determined by SEC.

LALLS data for the amine-capped polymers in cyclohexane, presented in Table 3, provide no evidence of association. The M_w values in cyclohexane are almost identical with those in THF. The only exception is sample 3N-3PBd15 for which the difference between the two values is greater than the typical statistical error of the method. The A_2 values in cyclohexane are always lower than in THF, probably because THF is a better solvent than cyclohexane for polybutadiene and/or because the amine groups associate to a small extent. Although the second virial coefficient is sensitive to association, and we cannot exclude this possibility (especially for 3N-3PBd15), we believe that the main reason for this behavior is the nature of the solvent. Data from linear polyisoprenes and block copolymers of styrene and isoprene with the dimethylamine functional groups support the conclusion that these groups are not polar enough to promote association.[21,25]

In the case of zwitterionic polymers strong association is observed in cyclohexane. The values of M_w measured by LALLS (Table 3) are much larger than those of the base polymers (Table 2). Representative examples from LALLS measurements for the amine-capped polymers and the corresponding zwitterion samples are given in Figure 6. The weight-average degree of association N_w is the ratio of M_w of the zwitterionic polymer, $(M_w)_{Zw}$, and of M_w of the amine precursor, $(M_w)_N$, $N_w = (M_w)_{Zw}/(M_w)_N$. The variation of N_w with $(M_w)_N$ is given in Figure 7. The molecular weight of the associated systems was measured by extrapolation to infinite dilution, where, of course, the associates would be completely dissociated. So what we actually obtain is the $(M_w)_{Zw}$ in the vicinity of the lowest measured concentration.

It is evident from Table 3 that (a) among the different series of polymers the degree of association decreases

Table 2. Molecular Characteristics of the Three-Arm PBd Stars with One, Two, or Three Dimethylamino End Groups in Toluene (MO) and THF (LALLS)

sample	$M_n \times 10^{-3}$ (PBd arm)	$M_n \times 10^{-3}$ (NPBd arm)	$M_n \times 10^{-3}$ (star)	$M_w \times 10^{-3}$ (star)	I(SEC)	$I = M_w/M_n$	f[a]	$A_2 \times 10^3$ (MO) (mL·mol·g^{-2})	$A_2 \times 10^3$ (LALLS) (mL·mol·g^{-2})
1N-3PBd8	7.1	9.1	23.8	25.8	1.05	1.08	3.1	2.36	2.12
1N-3PBd15	14.9	12.6	42.9	47.9	1.05	1.12	3.0	1.90	1.61
1N-3PBd20	15.7	14.3	46.9	49.8	1.05	1.06	3.1	1.73	1.91
1N-3PBd30	34.8	34.0	104.0	111.0	1.06	1.07	3.0	1.52	1.20
1N-3PBd40	45.5	35.6	131.4	149.7	1.06	1.14	3.1	1.38	1.37
2N-3PBd8	6.3	7.6	21.3	22.5	1.05	1.06	3.0	2.16	1.48
2N-3PBd15	13.1	14.7	43.4	46.5	1.04	1.07	3.1	1.90	1.98
2N-3PBd30	22.1	21.9	61.8	62.4	1.06	1.01	2.9	1.63	1.48
2N-3PBd40	35.0	30.7	89.0	99.0	1.06	1.11	2.8	1.47	1.37
3N-3PBd15		11.2	31.1	33.7	1.06	1.08	2.8	1.59	1.67
3N-3PBd25		23.2	62.5	67.4	1.06	1.08	2.7	1.56	1.51
3N-3PBd40		33.0	91.4	93.1	1.06	1.02	2.8	1.42	1.27

[a] Functionality, $f = M_n(\text{star})/M_n(\text{average of the arms})$.

Table 3. LALLS Results for the Amine-Capped (N) and Zwitterion-Capped (Zw) Stars in Cyclohexane

	$M_w \times 10^{-3}$		N_w[a]		$A_2 \times 10^3$ [b]	
sample	N	Zw	N	Zw	N	Zw
1-3PBd8	25.8	232.3	1.00	9.0	1.32	0.42
1-3PBd15	48.2	441.3	1.01	9.2	0.23	0.26
1-3PBd20	51.2	203.2	1.03	4.1	1.46	0.28
1-3PBd30	109.5	280.8	0.99	2.5	0.60	0.26
1-3PBd40	147.6	224.8	0.99	1.5	1.13	0.16
2-3PBd8	24.4	342.1	1.08	15.2	1.78	0.05
2-3PBd15	47.5	160.6	1.02	3.7	1.34	0.64
2-3PBd30	64.2	173.3	1.03	2.8	1.04	0.58
2-3PBd40	93.5	136.6	0.94	1.4	1.06	0.22
3-3PBd15	37.7	98.0	1.12	1.4	1.25	~0
3-3PBd25	69.6	174.3	1.03	1.9	1.08	0.10
3-3PBd40	88.2		0.95		1.14	

[a] Weight-average degree of association, $N_w = (M_w)_{N,Cycl}/(M_w)_{N,THF}$ for amine-capped stars and $N_w = (M_w)_{Zw,Cycl}/(M_w)_N$ for zwitterion-capped stars. [b] In mL·mol·g^{-2}.

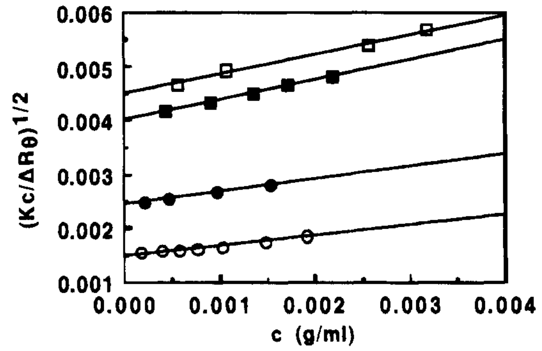


Figure 6. LALLS square-root plots for samples 1N-3PBd15 (□) and 2N-3PBd30 in THF (■), Zw-1N-3PBd15 (○), and Zw-2N-3PBd30 (●) in cyclohexane at 25 °C.

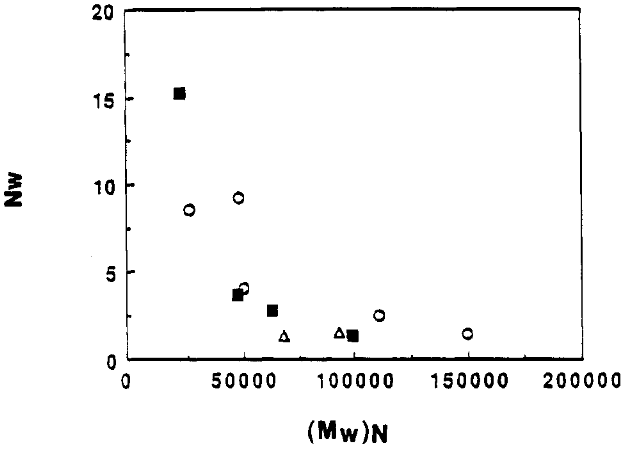


Figure 7. Weight-average degree of association N_w vs base molecular weight $(M_w)_N$ of the star polymers: Zw-1N-3PBd (○), Zw-2N-3PBd (■) and Zw-3N-3PBd (△).

with increasing number of functional groups and (b) among the samples with the same number of functional groups the degree of association increases with decreasing molecular weight of the base polymer. The first result can be seen as evidence of intramolecular association for the multifunctional samples. At the range of low concentrations used, the polymers tend to interact intramolecularly rather than intermolecularly. The second result can be explained by considering the existing excluded volume repulsions of the polymer chains.

Table 4. MO Results for the Zwitterion-Capped Stars in Cyclohexane

sample	$M_n \times 10^{-3}$	N_n[a]	$A_2 \times 10^3$ [b]
Zw-1N-3PBd15	182.8	4.3	0.5_7
Zw-1N-3PBd20	84.0	1.8	1.3
Zw-1N-3PBd30	124.2	1.2	1.1
Zw-1N-3PBd40	148.7	1.1_3	1.0
Zw-2N-3PBd15	74.8	1.7	1.1
Zw-2N-3PBd30	88.0	1.4	1.1
Zw-2N-3PBd40	85.4	0.9_6	0.4

[a] Number-average degree of association, $N_n = (M_n)Zw/(M_n)_N$. [b] In mL·mol·g^{-2}.

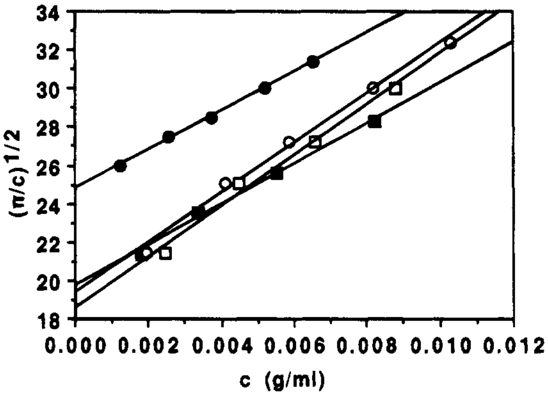


Figure 8. Osmometry square-root plots for samples 1N-3PBd20 (●) and 2N-3PBd30 (○) in toluene at 37 °C and Zw-1N-3PBd20 (■) and Zw-2N-3PBd30 (□) in cyclohexane at 25 °C.

The multifunctional samples tend to form gels in cyclohexane. The lowest concentration for which we have the formation of a gel is ≃10^{-2} g/mL for the difunctional and 10^{-3} g/mL for the trifunctional zwitterion-capped star polymers. In the case of Zw-3N-3PBd15, even at a concentration of 8×10^{-4} g/mL, the sample was not completely soluble, and consequently no measurements were performed. Taking into account that all measurements were carried out below the c_{gel} and that the degree of association is rather small for this series, we can conclude that there is a sharp transition from intermolecular to mainly intramolecular association.

The second virial coefficients for the zwitterion-capped polymers are decreased, almost by an order of magnitude, as compared with the corresponding amine precursors. This is a consequence of the increased molecular weights of the associates and the strong interactions between the polymer chains due to intermolecular and intramolecular association. It is noted that the lower values of the second virial coefficient appear for the samples with the lower degrees of association ($N_w < 2$). Although the intermolecular association is limited, for the concentration range used in this case the thermodynamic interactions are very strong due to the existing intramolecular association.

The number-average degree of association N_n, $N_n = (M_n)_{Zw}/(M_n)_N$ was calculated by using the membrane osmometry results. The values of $(M_n)_{Zw}$ and N_n in cyclohexane are given in Table 4. Example plots for some amine-capped and the corresponding zwitterion-capped polymers are shown in Figure 8. The variation of N_n with $(M_n)_N$ (Figure 9) shows a similar trend to that obtained between N_w and $(M_w)_N$. It is clear that the zwitterion associates are polydisperse (polydispersity index: 1.5–2.4). Unfortunately, because of the higher concentration range needed for osmometry, it was impossible to carry out experiments with the trifunctional samples.

The degrees of association for the star-shaped polymers examined are lower than those of linear ω-functionalized polybutadienes[44] with the same polar groups.

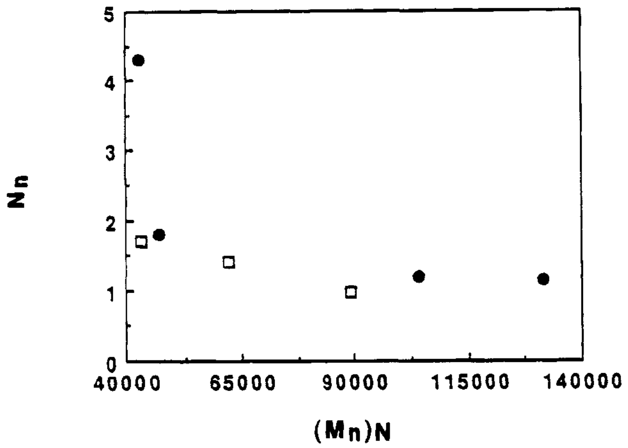


Figure 9. Number-average degree of association N_n vs base molecular weight of the star polymers: Zw-1N-3PBd (●) and Zw-2N-3PBd (□).

In the case of the monofunctional samples, the star structure probably prevents the association due to the steric hindrance caused by the unfunctionalized arms. For multifunctional samples there is a tendency for intramolecular association at very low concentration whereas in more concentrated solutions we have the formation of gels. The association behavior evidenced by viscometry and dynamic light scattering will be presented in a forthcoming paper.[45]

Conclusions

Three-arm polybutadiene stars with one, two, or three dimethylamine groups and narrow molecular weight distributions were prepared by anionic polymerization. The amine-capped polymers were transformed to sulfozwitterionic ones by reaction with cyclopropanesultone. Experimental data for the amine polymers do not provide evidence of association in cyclohexane whereas the corresponding zwitterion samples associate strongly in this solvent. The degree of association increases with decreasing number of functional groups and with decreasing molecular weight for samples with the same number of functional groups. Osmometry and LALLS show that the associates are polydisperse. The lower degrees of association, as compared with the corresponding linear ω-functionalized PBd are probably due to the existence of intramolecular association (difunctional and trifunctional species) and to the steric hindrance caused by the unfunctionalized branches (monofunctional species). Multifunctional samples, especially those with three zwitterion groups, form gels, even at very low concentrations.

References and Notes

(1) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143.
(2) Hegedus, R. D.; Lenz, R. W. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 367.
(3) Lantman, C. W.; MacKnight, J. W.; Peiffer, D. G.; Sinha, S. K.; Lundberg, R. D. *Macromolecules* **1987**, *20*, 1096.
(4) Hara, M.; Wu, J. *Multiphase Polymers: Blends and Ionomers*; Utracki, L. A., Weiss, R. A., Eds.; ACS Symposium Series 395; American Chemcial Society: Washington, DC, 1988, Chapter 19.
(5) Charlier, P.; Jérôme, R.; Teyssié, P. *Macromolecules* **1990**, *23*, 1831.
(6) Broze, G.; Jérôme, R.; Teyssié, P. *Macromolecules* **1982**, *15*, 920.
(7) Charlier, P.; Jérôme, R.; Teyssié, P.; Utracki, L. A. *Macromolecules* **1990**, *23*, 3313.
(8) Williams, G. E.; Russell, T. P.; Jérôme, R.; Horrion, J. *Macromolecules* **1986**, *19*, 2877.
(9) Joanny, J. F. *Polymer* **1980**, *21*, 71.
(10) Witten, T. A., Jr.; Cohen, M. H. *Macromolecules* **1985**, *18*, 1915.
(11) Cates, M. E.; Witten, T. A. *Macromolecules* **1986**, *19*, 732.
(12) Wang, Z.-G.; Safran, S. A. *J. Chem. Phys.* **1988**, *89*, 5323.
(13) Brédas, J. L.; Chance, R. R.; Silbey, R. *Macromolecules* **1988**, *21*, 1633.
(14) Nagata, N.; Kobatake, T.; Watanabe, H.; Veda, A.; Yoshioka, A. *Rubber Chem. Technol.* **1987**, *60*, 837.
(15) French, D. M. *Rubber Chem. Technol.* **1969**, *42*, 71.
(16) Worsfold, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2237.
(17) Worsfold, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2271.
(18) Quirk, R. P.; Yin, J.; Guo, S.-H.; Hu, X.-W.; Summers, G.; Kim, J.; Zhu, L.-F.; Schock, L. E. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 47.
(19) Quirk, R. P.; Kim, J. *Macromolecules* **1991**, *24*, 4515.
(20) Möller, M.; Omeis, J.; Mühleisen, E. In *Reversible Polymeric Gels and Related Systems*; Russo, P. S., Ed.; ACS Symposium Series 350; American Chemical Society: Washington, DC, 1987.
(21) Davidson, N. S.; Fetters, L. J.; Funk, W. J.; Graessley, W. W.; Hadjichristidis, N. *Macromolecules* **1988**, *21*, 112.
(22) Fetters, L. J.; Graessley, W. W.; Hadjichristidis, N.; Kiss, A. D.; Pearson, A. D.; Younghouse, L. B. *Macromolecules* **1988**, *21*, 1644.
(23) Shen, Y.; Safinya, C. R.; Fetters, L. J.; Adam, M.; Witten, T.; Hadjichristidis, N. *Phys. Rev.* **1991**, *43*, 1886.
(24) Hadjichristidis, N. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 47.
(25) Pispas, S.; Hadjichristidis, N. *Macromolecules* **1994**, *27*, 1891.
(26) Pispas, S.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1994**, *27*, 6307.
(27) Kennedy, J. P.; Ross, L. R.; Lackey, J. E.; Nuyken, O. *Polym. Bull.* **1981**, *4*, 67.
(28) Mohajer, Y.; Tyagi, T.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *Polym. Bull.* **1982**, *8*, 47.
(29) Bagrodia, S.; Mohajer, Y.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *Polym. Bull.* **1982**, *8*, 281.
(30) Bagrodia, S.; Mohajer, Y.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *Polym. Bull.* **1983**, *9*, 174.
(31) Bagrodia, S.; Pisipati, R.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *J. Appl. Polym. Sci.* **1984**, *29*, 3065.
(32) Bagrodia, S.; Wilkes, G. L.; Kennedy, J. P. *J. Appl. Polym. Sci.* **1985**, *30*, 2179.
(33) Storey, R. F.; George, S. E.; Nelson, M. E. *Macromolecules* **1991**, *24*, 2920.
(34) Khasat, N.; Pennisi, R. W.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1988**, *21*, 1100.
(35) Iatrou, H.; Siakali-Kioulafa, E.; Hadjichristidis, N.; Roovers, J.; Mays, J. W. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(36) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.
(37) Roovers, J.; Toporowski, P. *Macromolecules* **1983**, *16*, 843.
(38) Pispas, S.; Pitsikalis, M.; Hadjichristidis, N.; Dardani, P.; Morandi, F. *Polymer*, accepted.
(39) Chen, X.; Xu, Z.; Hadjichristidis, N.; Fetters, L. J.; Carella, J.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 777.
(40) (a) Richards, D. A.; Stewart, M. J. *Polymer* **1983**, *24*, 883. (b) van der Velden, G.P.M.; Fetters, L. J. *Macromolecules* **1990**, *23*, 2470.
(41) Hadjichristidis, N.; Roovers, J. E. L. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2521.
(42) Hadjichristidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* **1978**, *11*, 668.
(43) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.
(44) Pitsikalis, M.; Siakali-Kioulafa, E.; Hadjichristidis, N. *J. Polym. Sci., Polym. Phys. Ed.*, submitted for publication.
(45) Pitsikalis, M.; Hadjichristidis, N.; Mays, J. W. *Macromolecules*, to be submitted.

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