

MODEL POLYMERS WITH DIMETHYLAMINE AND SULFOZWITTERIONIC END-GROUPS. SYNTHESIS AND SELF ASSEMBLY IN SOLUTION AND IN BULK

MODELNI POLIMERI Z DIMETILAMINSKIMI IN SULFOZWITTERIJSKIMI KONČNIMI SKUPINAMI

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The dilute solution and bulk properties of a variety of well-defined polymers of different architectures (linear homopolymers, diblock and triblock copolymers and star homopolymers) having dimethylamine and sulfobetaine end groups mainly synthesized in our laboratory are reviewed. The end functionalized polymers were synthesized by means of anionic polymerization high vacuum techniques, using 3-dimethylaminopropyl-lithium as initiator for the introduction of the dimethylamine group at the chain end. This group was converted to sulfozwitterionic by reaction with cyclopropanesultone. Extensive molecular characterization proved the high homogeneity of these model materials. Their aggregation properties in dilute solutions, of solvents of different polarity and selectivity towards different parts of the molecules, were studied by viscometry, static and dynamic light scattering. The ω -functionalized polystyrenes and the block copolymers of styrene have a much lower degree of association, than the homopolydienes, probably due to the polarizability of the phenyl group. The bulk properties of end-functionalized homopolymers and diblocks were studied by SAXS, reology and dielectric spectroscopy revealing new features of self organization at this low ionic content and extraordinary phase behavior at high temperatures. The adsorption behavior of stars with different number of functionalized arms in dilute solutions was also investigated by ellipsometry showing different behavior compared to linear polymers.

Key words: end-functionalized polymers, anionic polymerization, macromolecular architecture, association, phase separation, adsorption

V delu je podan pregled lastnosti vrste dobro definiranih polimerov z različnimi arhitekturami (linearni homopolimeri, diblok in triblok kopolimeri, zvezdasti homopolimeri) z dimetilaminskimi in sulfobetajnskimi končnimi skupinami, v razredčenih raztopinah in v masi. Polimere s funkcionalnimi končnimi skupinami smo sintetizirali z anionsko polimerizacijo z visoko-vakuumsko tehniko. Z iniciatorjem 3-dimetilaminopropilijem smo na konec verige uvedli dimetilaminsko skupino, ki smo jo z reakcijo s ciklopropanosultonom prevedli v sulfozwitterionsko. Temeljita molekularna karakterizacija je potrdila, da so sintetizirani modelni materiali zelo homogeni. Z viskozimetrijo ter statičnim in dinamičnim sipanjem svetlobe smo raziskali njihove agregacijske lastnosti v razredčenih raztopinah, v toplih različne polarnosti in selektivnosti do določenih delov molekul. ω -funkcionalizirani polistireni in blok kopolimeri stirena imajo, verjetno zaradi polarizabilnosti fenilne skupine, mnogo nižjo stopnjo asociacije kot homopolidieni. S SAXS reologijo in z dielektrično spektroskopijo smo študirali lastnosti ω -funkcionaliziranih homopolimerov in diblokov v masi ter ugotovili nove oblike samoorganiziranosti pri tej nizki koncentraciji ionov ter nenavadno obnašanje faz pri visoki temperaturi. Z elipsometrijo smo raziskali tudi adsorpcijske lastnosti zvezdastih polimerov z različnim številom funkcionaliziranih vej v razredčenih raztopinah in ugotovili, da se razlikujejo od lastnosti linearnih polimerov.

Ključne besede: polimeri s funkcionalnimi končnimi skupinami (ω -funkcionalizirani polimeri), anionska polimerizacija, makromolekularna arhitektura, asociacija, fazna separacija, adsorpcija

1 INTRODUCTION

The presence of even a few highly polar groups distributed along or fixed at the ends of nonpolar chains changes dramatically the properties of polymers¹⁻⁷. These changes are caused by association of polar groups in the nonpolar environment of the hydrocarbon chains in the bulk or of the aliphatic solvents in solution.

The least complicated examples of polymeric associating species are chains with one polar group⁸⁻⁹. These simple materials offer an essential starting point for testing theories and establishing the basic structure-properties relationships, which will help to design associating polymers for practical applications.

Although many routes exist for the synthesis of end functionalized polymers¹⁰⁻¹², living anionic polymerization has been proven to be the most efficient method for synthesizing well defined macromolecules^{13,14}, since it

gives the possibility to control many structural variables including placement of the ionic groups.

This review will be focused on the dilute solution and bulk properties of dimethylamine and sulfozwitterionic end-functionalized polymers having different architectures (linear homopolymers, diblock and triblock copolymers and star polymers with a different number of functional groups), synthesized mainly in our laboratory.

2 SYNTHESIS AND CHARACTERIZATION Homopolymers

3-Dimethylaminopropyl-lithium (DMAPLi) was used as initiator for the introduction of the dimethylamine group at the end of the polymer chain in all cases. DMAPLi was prepared by reaction of the corresponding chloride (DMAPCl) and Li dispersion according to Stewart et al.¹⁵. Styrene (St), Isoprene (Is) and butadiene

(Bd) were polymerized with DMAPLi. The molecular weight distributions are low in the case of polydienes. Stoichiometric molecular weights are in very good agreement with the number average molecular weights, measured by osmometry. These results indicate that DMAPLi is an efficient initiator for the polymerization of isoprene and butadiene.

The microstructure of the polydienes was investigated using $^1\text{H-NMR}$ spectroscopy. The results clearly show an increase of the vinyl content with decreasing chain length, due to the presence of the polar dimethylamine group in the initiator.

The slow initiation rate was readily observed during the polymerization of St by the gradual appearance of the orange color¹⁶, which is characteristic of the living polystyryllithium chains. This fact in combination with the very fast propagation rate for the polymerization of St resulted in very broad molecular weight distributions ($I=1.23-1.27$). In addition, the $M_n(\text{SEC})$ of samples with stoichiometric molecular weights $M_s < 9300$ were much higher than the stoichiometric ones, with the difference being higher by decreasing M_s . This behaviour can be explained by partial consumption of the initiator. This was verified by the subsequent addition of Is, which produced polymers having bimodal distribution (figure 1). The lower molecular weight peak, not seen by the UV detector, corresponds to NPI homopolymer, produced by the DMAPLi, which remained unreacted during the polymerization of St. The higher molecular weight peak is attributed to the NPSt-b-PI block copolymer with the amine group at the PSt chain end, produced by the crossover reaction of NPStLi with Is. Addition of THF to the mixture of St and DMAPLi ($[\text{THF}]/[\text{Li}] > 3$) gave polymers with close agreement between M_s and M_n and lower polydispersities.

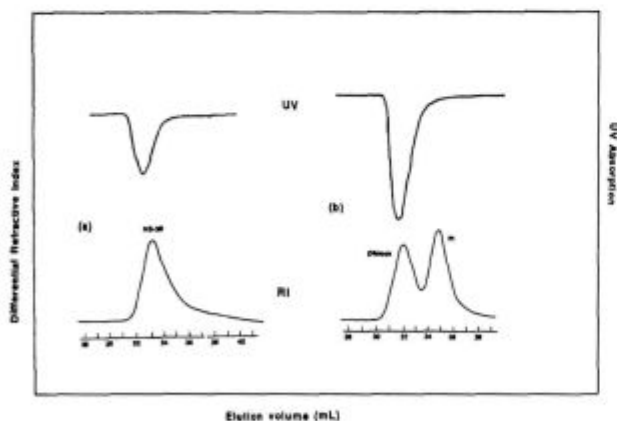
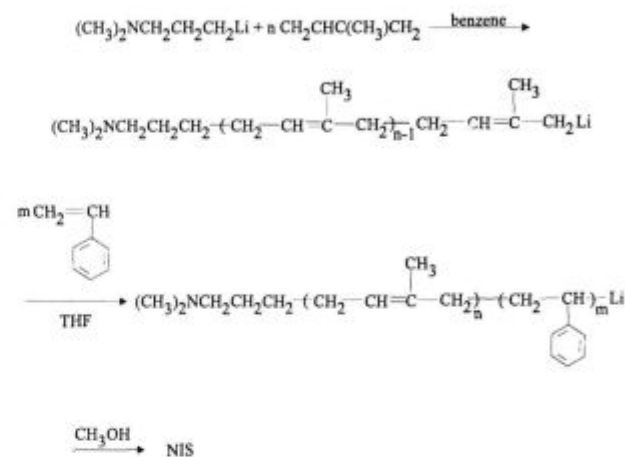


Figure 1: SEC chromatograms of (a) NS-3B (purified DMAPLi; polymerization in pure benzene) and (b) NS-3B after the addition of isoprene (first peak, diblock formed; second peak, homopolyisoprene formed by reaction of isoprene with unreacted DMAPLi). The UV detector sees only the PS part

Slika 1: SEC kromatogrami (a) NS-3B (očišćen DMAPLi; polimerizacija v čistom benzenu) in (b) NS-3B po dodatku izoprena (prvi vrh ustreza diblok kopolimeru; drugi vrh ustreza homopolizoprenu, ki nastane v reakciji med izoprenom in nezreagiranim DMAPLi). UV detektor zazna samo polistirenski del blok kopolimera

3 DIBLOCK AND TRIBLOCK COPOLYMERS

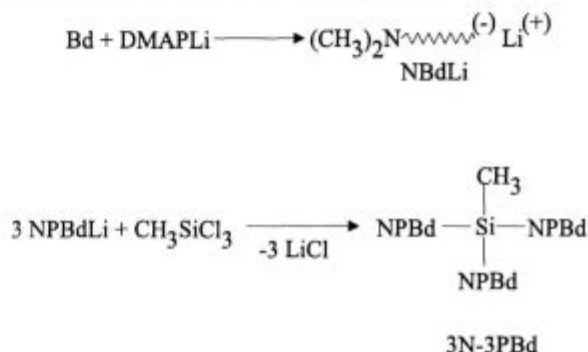
Block copolymers of styrene and isoprene having dimethylamine end-groups at the one or the other chain end were prepared using DMAPLi and sequential addition of monomers¹⁷. When Is is polymerized first, a small amount of THF is added after the polymerization of the diene is completed to accelerate the crossover reaction with St. The reaction scheme is the following:



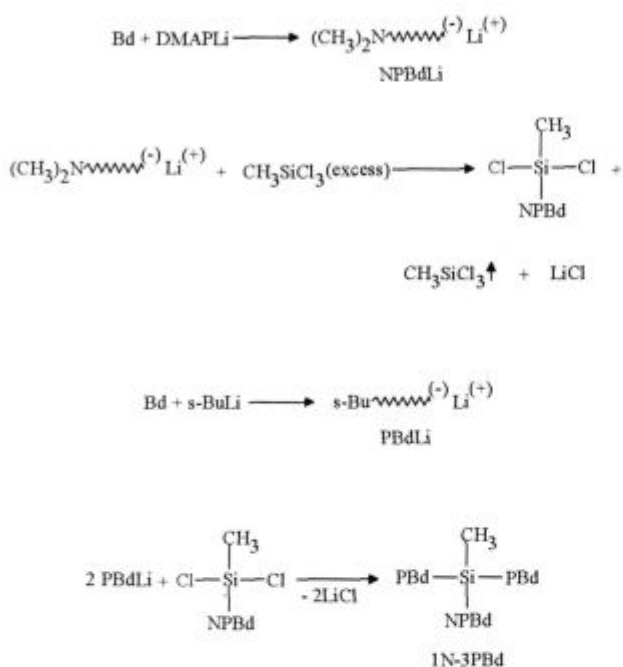
Triblock copolymers, having dimethylamine groups at both chain ends were prepared by coupling diblock chains with dimethyldichlorosilane, $(\text{CH}_3)_2\text{SiCl}_2$. The products are characterized by compositional and chemical homogeneity and low molecular weight distributions. The samples are designated with the letter N corresponding to the end-amine group, followed by the sequence of blocks starting with the block at which the functional group is attached.

4 ω -FUNCTIONALIZED STAR POLYISOPRENES AND Mono-, Di- AND Tri- ω -FUNCTIONALIZED THREE ARM STAR POLYBUTADIENES

Three and twelve arm PI stars¹⁸ and three arm star PBd with all ends functionalized with dimethylamine groups¹⁹ were synthesized by the reaction of end-functionalized living polymers with suitable chlorosilanes. As an example the 3-arm polybutadienes have been prepared according to the following scheme:



Three arm stars PBd with one or two end-amine groups were prepared using controlled chlorosilane chemistry¹⁹. The presence of one or two functional groups is denoted by the symbols 1N- and 2N- respectively, whereas the symbol 3PBd denotes a three arm star PBd. So 1N-3PBd is a three arm star PBd with one end-amine group. The following numbers differentiate samples of the same series. A schematic representation of the reaction sequence used for the synthesis of samples 1N-3PBd is shown below:



A living end-functionalized PBd chain was prepared in benzene using DMAPLi as initiator. The living polymer solution was added to a large excess of methyltrichlorosilane (Si-Cl/C-Li ≈ 100/1) in order to prepare the methyltrichlorosilane-capped PBd. The excess of linking agent was removed under vacuum line conditions. The polymer was repeatedly redissolved and pumped to extract traces of silane from the bulk polymer. Finally benzene was distilled into the reactor to dissolve the ω-methyltrichlorosilane PBd arm.

The next step involved the synthesis of the unfunctionalized arm, using *s*-BuLi as initiator. A small excess of this living polymer was coupled with the macro-molecular linking agent to produce the final product. Termination of the residual active anions with degassed MeOH and subsequent fractionation to remove the excess PBd arm gave the pure 1N-3PBd star polymer.

A similar procedure is followed for the synthesis of 2N-3PBd stars, starting from the reaction of the living unfunctionalized arm with excess methyltrichlorosilane followed, after the removal of the excess linking agent, by the coupling reaction of the dichlorosilane-capped arm with a small excess of the amine-functionalized living arm. All these procedures were monitored by SEC.

In the case of samples with low arm molecular weight ($M_n < 10^4$) and in order to prevent the formation of the diadduct the steric hindrance of the living arm PBd was increased by reaction with diphenylethylene (DPE). A few drops of THF were added to accelerate the cross-over reaction. The coupling reaction was minimized using this procedure giving less than 3% of the byproduct.

The molecular characteristics of representative samples synthesized as described above are given in **Table I**.

Table I: Molecular characteristics of diblock, triblock and three-arm PBd stars with one, two, or three dimethylamino end groups

Tabela I: Molekularne lastnosti zvezdastih PBd polimerov z dvema blokoma, s tremi bloki in tremi vejami, z eno, dvema ali tremi dimetilaminskimi končnimi skupinami

Sample	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$I = M_w/M_n$ (SEC)	%wt PS
NPI	4.56	4.53	1.04	
3NPI	7.2	6.6	1.05	
NIS-3	2.44	2.25	1.06	28
NSI-1	6.96	6.12	1.06	30
NSISN-1	7.63	7.02	1.05	36
NISIN-1	6.98	6.27	1.05	27
1N-3PBd30	11.1	10.4	1.06	
2N-3PBd30	62.4	61.8	1.06	
3N-3PBd40	93.1	91.4	1.06	

5 POST-POLYMERIZATION REACTION OF THE AMINE-FUNCTIONALIZED POLYMERS

The amine end groups can be easily transformed to ionic dipoles by reaction with 1,3 cyclopropane sultone^{20,21}, illustrated in the following scheme:



The reaction takes place in dilute THF solutions (2-3 w/v%) at 70°C for several days using an excess of the sultone over the amine groups (sultone/amine = 10/1). For the PBd samples inert atmosphere was used. Under these conditions this post-polymerization reaction is free of side reactions (crosslinking, degradation etc.) as was verified by SEC. Similar peaks with the corresponding amine-capped polymers were observed in CHCl₃ in all cases.

It is difficult to determine the extent of the conversion of the *t*-amine groups to sulfobetaines due to the low concentration of these groups in the polymer chains. However, qualitative results by ¹H-NMR show that the reaction yield is very high^{17,22}. In **figure 2** the ¹H-NMR spectra of linear block copolymer NIS-5 and the corresponding zwitterion sample are given. The peak at 2.2 ppm is assigned to the methyl protons of the carbons attached to the nitrogen atom. This peak has completely disappeared after the reaction with 1,3 cyclopropane sul-

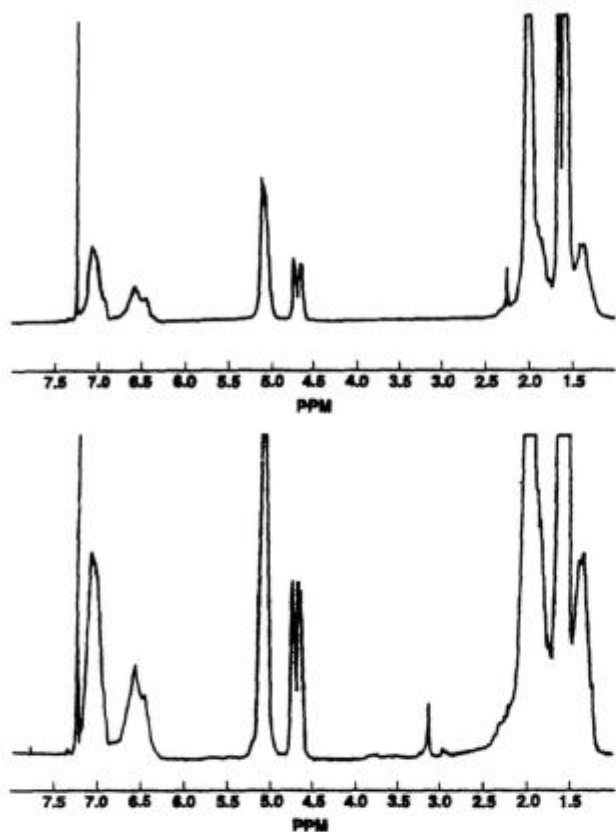


Figure 2: ¹H-NMR spectra of samples NIS-5 (top) and ZwIS-5 (bottom) in CDCl₃
 Slika 2: ¹H NMR spektri vzorcev NIS-5 (zgornji) in ZwIS-5 (spodnji spekter) v CDCl₃

tone and two new peaks at 3.15 and 2.95 ppm have emerged. These peaks are assigned to the methyl protons attached to the positively charged nitrogen atom of the zwitterionic group and to the methylene protons of the carbon attached to the sulfur atom respectively^{21,23}.

6 DILUTE SOLUTION AND BULK PROPERTIES Homopolymers

The dilute solution properties of ω-functionalized linear homopolymers were studied by membrane osmometry (MO), low angle laser light scattering (LALLS) viscometry, and dynamic light scattering (DLS) in various non-polar solvents^{18,24,25}. The conclusions obtained from this study are the following:

- a) The dimethylamine-capped samples present no evidence of association in non-polar solvents (cyclohexane, CCl₄, toluene)
- b) The zwitterion-capped samples form large aggregates in these solvents with aggregation numbers increasing with decreasing molecular weight of the parent material. However, aggregation numbers for PS homopolymers are lower than those obtained for poly-

- diene homopolymers probably because of the solvating effect of phenyl rings on the dipolar groups
- c) The aggregates are polydisperse as concluded by LALLS, MO and DLS measurements
- d) The associates behave hydrodynamically as star polymers as evidenced by the increasing k_H values with increasing degree of association and by the good agreement between experimental aggregation numbers and those calculated assuming the star model
- e) The linear head packing model describes fairly well the structures of the associates.

Detailed studies by small angle x-ray scattering (SAXS) were performed on low molecular weight zwitterion-capped polyisoprenes²⁶. For samples having $14000 < M_w < 28000$ the scattering profiles show that the aggregates form a body-centered cubic lattice.

Figure 3 shows the corresponding scattering profiles for the lower molecular weight samples ($2200 < M_w < 4650$). The peaks can be indexed on a two dimensional hexagonal lattice of tubes. In other words the aggregates have a tubular structure with the tubes closed packed on a two dimensional hexagonal lattice with crystalline order. The core is formed by dipoles which are arranged in an antiparallel configuration as shown in figure 4.

It is characteristic that a very small weight fraction of ionic species (3.5-7.5%) is able to promote a hexagonal cylinder morphology with long range order in contrast to usual block copolymers.

The viscoelastic behavior in the melt state of end-functionalized polyisoprenes was also investigated²⁷. The amine-capped samples behave more or less as conventional polyisoprenes indicating that only weak associa-

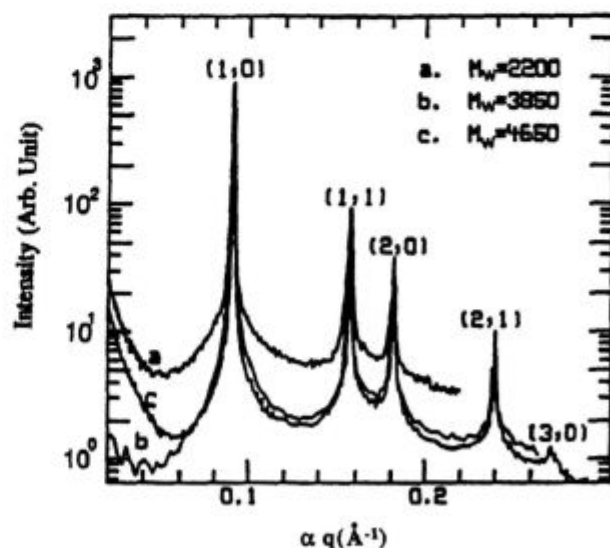


Figure 3: X-ray scattering profiles of zwitterion-capped polyisoprene samples with molecular weights of 4650, 3850, and 2200. The profiles of the last two samples were shifted by a factor (α) to make the first peak positions overlap

Slika 3: Krivulje sipanja rentgenskih žarkov vzorcev poliizoprena s končnimi zwitterionskimi skupinami z molskimi masami 4650 (c), 3850 (b) in 2200 g/mol (a). Zaradi lažje primerjave krivulj sta krivulji zadnjih dveh vzorcev premaknjeni za faktor (α)

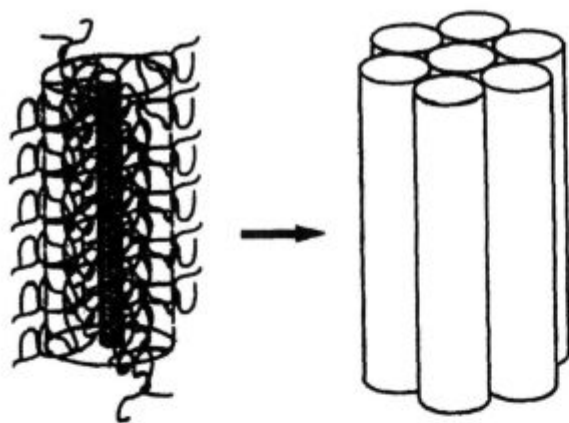


Figure 4: A schematic representation of the formation of two-dimensional lattices of close-packed tubular aggregates

Slika 4: Shematska predstavitev nastanka dvodimenzionalnih mrež tesno zloženih cevastih agregatov

tion may exist in the melt state. The situation is very different for the zwitterion-capped polymers with the dynamic moduli broadened and shifted to much lower frequencies. For samples with high base molecular weights the viscoelastic behaviour more closely resembles the behaviour of conventional star polymers.

Samples with intermediate and lower molecular weights show a second relaxation regime at very low frequencies. A characteristic example is given in figure 5. It is observed that some resemblance exist between the zwitterion and star polymer only at intermediate and high frequencies.

The viscosities of the zwitterion polymers, especially of low and intermediate molecular weights are much larger than those predicted assuming the star model. Consequently, it is reasonable to consider that aggregates

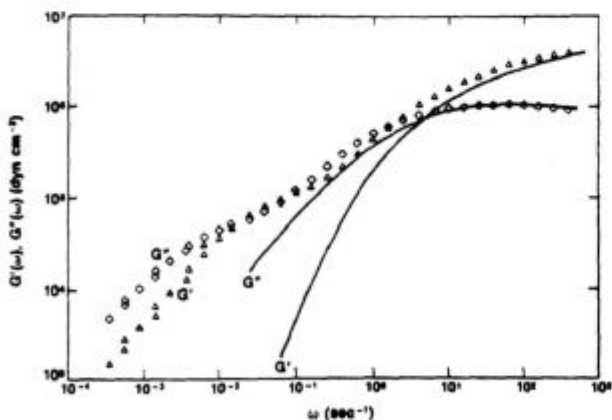


Figure 5: Comparison of dynamic moduli for a four-arm polyisoprene star and a monofunctional zwitterion polyisoprene in the melt state at 25°C. Data for the star ($M_0=4.4 \times 10^4$) are shown by the solid lines; the points are data for a sample with $M_0=4.61 \times 10^4$

Slika 5: Primerjava dinamičnih modulov zvezdastega poliizoprena s štirimi vejami in monofunkcionalnega zwitterionskega poliizoprena v talini pri 25°C. Neprekinjena črta - zvezdasti poliizopren ($M_0=4.4 \times 10^4$), točke - vzorec z $M_0=4.61 \times 10^4$

have extended morphologies (lamellae, strings etc.). Only in the case of low aggregation numbers, observed for samples of high base molecular weight, the behavior is similar to those of star polymers because the core size is rather small and can be considered as the star's center. The extended structures are delicate in a mechanical sense making it possible to explain the remarkable strain sensitivity observed at low frequencies. It is noted that there is close agreement with the results obtained by melt rheology and SAXS.

7 ω -FUNCTIONALIZED BLOCK COPOLYMERS OF STYRENE AND ISOPRENE

The association behavior of end-functionalized diblock and triblock copolymers of isoprene and styrene was studied in CCl_4 , which is a nonpolar and good solvent for both blocks^{17,28}. The aggregation numbers, N_w are almost the same whether the zwitterion group is linked at the PI or the PS chain end. Their value depends strongly on the M_w of the base polymer. N_w decreases with increasing molecular weight of the precursor polymer, M_0 . The variation of N_w with M_0 for the case of ZwPI in cyclohexane¹⁸ and CCl_4 ¹⁷, PS in CCl_4 ²⁷ di- and triblock copolymers in CCl_4 ¹⁷ is given in figure 6. The aggregation numbers for ZwPI are lower in CCl_4 than in cyclohexane due to the higher polarizability of the former solvent. Another point to be noticed is that the degrees of association of copolymers are closer to those determined for the ZwPS samples than to those of ZwPI samples in CCl_4 . The aromatic rings, due to their high polarizability cause some kind of solvation, and lead to reduced N_w values. The aggregation numbers are almost the same for the monofunctional and difunctional samples. This is rather surprising, since the difunctional polymers form gels at concentrations lower than c_{gel}

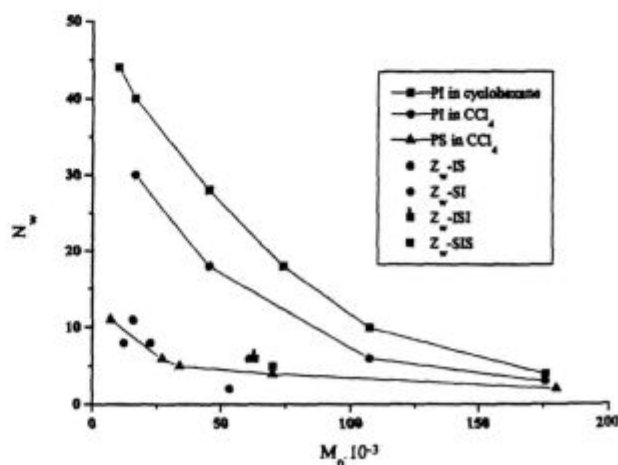


Figure 6: Dependence of the weight average aggregation number, N_w from the base molecular weight, M_0 for various polymer series

Slika 6: Odvisnost utežnega povprečja števila agregacije N_w od molekulske mase M_0 za različne serije polimerov

($c_{gel}=0.5\text{ c}^*$) and can be seen as evidence of intramolecular association in very dilute solutions.

DLS was used to study the hydrodynamic properties of the end-functionalized copolymers. The zwitterionic polymers have a substantially different behaviour than their precursors, due to the formation of aggregates in CCl_4 . The values of diffusion coefficient at infinite dilution, D_0 are lower, the R_H values higher, and the aggregates are polydisperse. The k_D values are negative in most cases, due to the aggregation process and are consistent with the low A_2 values obtained by LALLS.

Viscosity measurements were also performed to complement the DLS data. The $[\eta]$ values for the zwitterionic samples are considerably higher than those for the amine-capped samples and the reduced viscosity vs concentration plots are not always linear. The Huggins plots are concave upwards in some cases and especially for the difunctional samples.

The nonlinear dependence of the reduced viscosity on concentration is an indication that the association number changes by increasing concentration, something which is expected to be more pronounced in the case of the difunctional triblocks.

The stability of aggregates was tested by adding small amounts of an alcohol, namely 2-methylcyclohexanol (at 1% and 5% content). The association is reduced in the presence of the alcohol, but even by 5% alcohol samples remained aggregated. With increasing alcohol content the aggregation numbers decreased, the A_2 values increased and the k_H values are decreased also.

SAXS, rheology, and dielectric spectroscopy were used to study the statics and dynamics of the end-functionalized block copolymer^{29,30}. SAXS profiles from amine and the corresponding zwitterion-capped samples confirm the existence of ionic aggregation. A characteristic example is given in **figure 7**. The following features were observed:

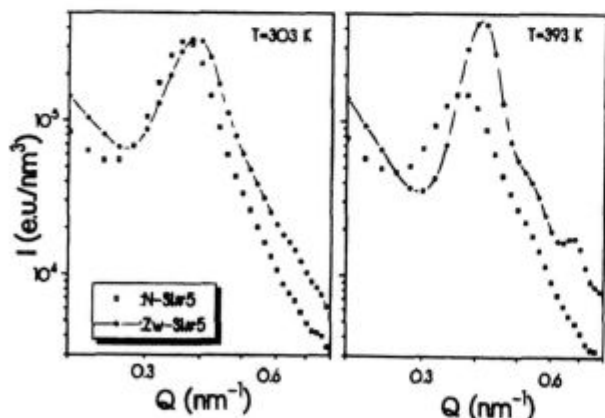


Figure 7: SAXS profiles for two ω -functionalized IS diblock copolymers at $T=303\text{ K}$. Data were corrected for density fluctuations and the intensities are given in absolute units

Slika 7: SAXS krivulje dveh ω -funkcionaliziranih izopren-stirenskih (IS) diblok kopolimerov pri $T=303\text{ K}$. Pri podatkih so upoštevene fluktuacije gostote, intenzitete so podane v absolutnih enotah

- a background originating from density and concentration fluctuations
- an excess intensity at low Q related to heterogeneities with long correlation lengths in the case of ionomers³¹
- the microdomain peak³² characteristic of the microphase separation process between PI and PS phases and
- the peak related to the polar groups, which emerged in the case of the zwitterionic sample.

The last three characteristics are temperature dependent with the aggregate peak intensity being much less sensitive to changes of temperature for the specific experiment temperature range. The microdomain peak intensity has a similar temperature dependence for both the amine and the zwitterion-capped copolymers.

A completely different behavior is observed when the functional group is attached to the PS chain-end, as shown in **figure 8**. The microdomain peak dominates the scattering pattern in this case. The peak increases in intensity, sharpens, and moves to slightly higher Q values with increasing temperature. The absence of any dissolution process clearly indicates that the microdomain structure is stabilized by the ionic aggregates. In the case of ZwSI samples the ionic groups are trapped within the PS phase without being able to aggregate. The increase of temperature increases the mobility of the polar groups leading to the formation of aggregates within the "hard" phase. This is schematically shown in **figure 9** for both systems, ZwIS and ZwSI. As a consequence the incompatibility of PI and PS is enhanced and a completely different phase behavior is observed. So only by changing the position of the polar group, from the PI to the PS chain-end it is possible to change the phase diagram.

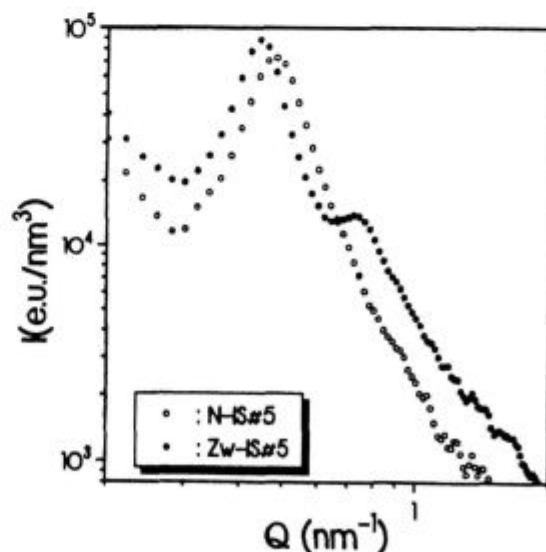


Figure 8: Comparison of the SAXS profiles for the dimethylamino- and zwitterion-substituted ω -functionalized copolymers at two temperatures

Slika 8: Primerjava SAXS krivulj dimetilamino- in zwitterionsko substituiranih ω -funkcionaliziranih kopolimerov pri dveh temperaturah

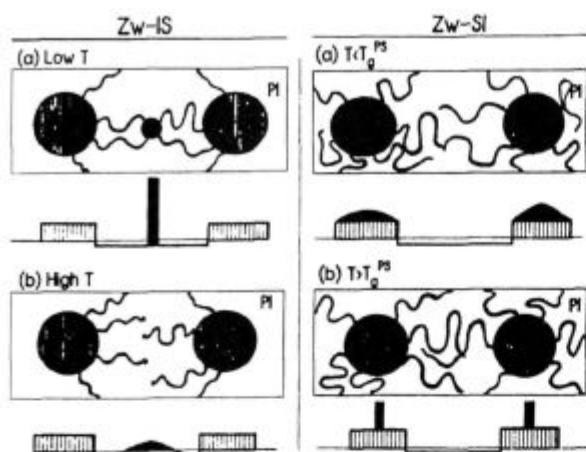


Figure 9: Schematic illustration of the microstructures in ω -functionalized SI block copolymers, showing the Zw-IS (left) and Zw-SI (right) cases at low (upper) and high (lower) temperatures. The corresponding electron density distributions are also shown

Slika 9: Shematska predstavitev mikrostrukture ω -funkcionaliziranih SI blokkopolimerov pri nižji (zgoraj) in višji temperaturi (spodaj) za Zw-IS (levo) in Zw-SI (desno). Prikazana je tudi ustrezna porazdelitev elektronske gostote

The conclusions derived by SAXS studies were confirmed by rheology. In the case of the zwitterionic copolymers an extension of the rubbery plateau is observed. This behaviour is explained considering that the aggregates act as physical crosslinks within the PI phase. Furthermore, within the temperature range investigated no sign of an order-disorder transition was observed in agreement with SAXS results, meaning that the cubic microdomain structure is stable up to high temperatures.

Dielectric spectroscopy also offers the means to verify the conclusions drawn so far through the selective probing of the PI chains. In the case of ZwIS copolymers in addition to the fast segmental and the slow normal mode an intermediate process, with activation parameters which are reminiscent of the segmental process, is observed. This intermediate process arises from regions of the reduced mobility created around the aggregates impeding the motion of the PI chains in their immediate environment. However differential scanning calorimetry, DSC is not so sensitive and the size of these regions very small in order to detect an intermediate Tg value, although an increase on the Tg of the polyisoprene block has been observed at low molecular weights³³.

The combination of the association process caused by the presence of polar groups in a nonpolar solvent with the micellization procedure, promoted in selective solvents leads to interesting solution behavior. The dilute solution properties of ω -functionalized diblock copolymers having dimethylamine or zwitterion groups at the PS chain-end were studied in n-decane a nonpolar selective solvent for the PI blocks³⁴.

The presence of the polar groups introduces another factor capable to enhance the aggregation numbers for the zwitterionic samples in n-decane. Much lower N_w

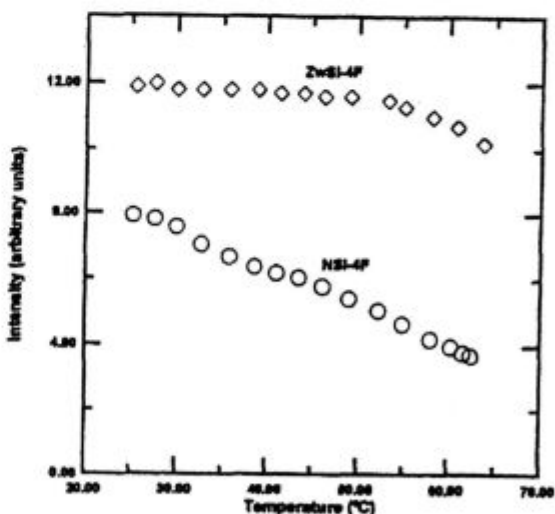
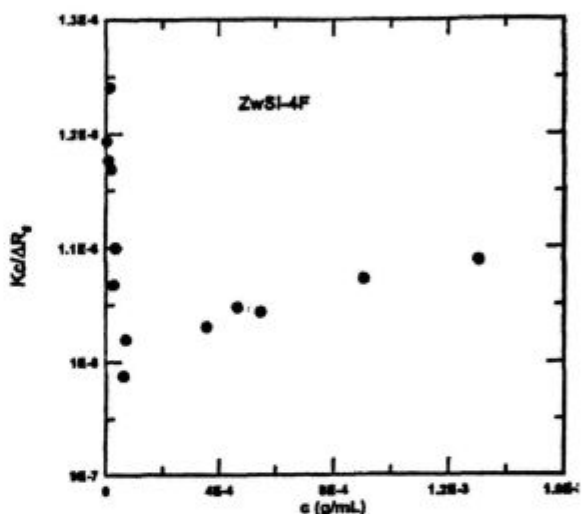
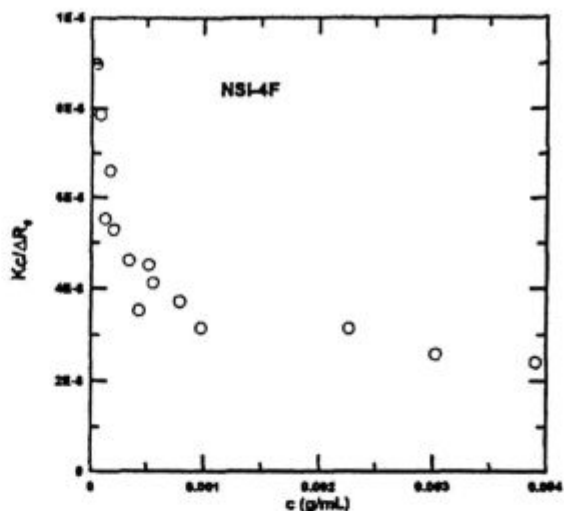


Figure 10: $Kc/\Delta R_{\theta}$ vs concentration plots given for (a) sample NSI-4F and (b) sample ZwSI-4F in n-decane at 25°C. (c) Intensity vs temperature plot for the same samples at $c=2.800 \times 10^{-3}$ g/mL for NSI-4F and $c=1.629 \times 10^{-3}$ g/mL for ZwSI-4F

Slika 10: $Kc/\Delta R_{\theta}$ v odvisnosti od koncentracije za vzorca (a) NSI-4F in (b) ZwSI-4F v n-dekanu pri 25°C; (c) odvisnost intenzitete od temperature za NSI-4F pri $c=2,8 \times 10^{-3}$ g/mL in za ZwSI-4F pri $c=1,629 \times 10^{-3}$ g/mL

values were observed for the amine-capped copolymers, meaning that the amine groups are not polar enough to enhance the association process. Typical LALLS plots are given in figure 10.

From DLS measurements negative k_D values were obtained for the amine-capped polymers as expected having in mind the negative A_2 values. For the zwitterionic samples the k_D values were positive meaning that the equilibrium is shifted in favor of the micelles.

Viscometry measurements were also performed. The Huggins coefficients increase with increasing molecular weight for the amine-capped polymers. This behavior is consistent with a star-like structure. For the zwitterionic samples constant k_H values, around 1.1 were obtained, meaning that rather compact structures exist in solution.

The R_v and R_H values are identical within experimental error for the amine polymers but for the zwitterionic polymers R_H is much higher than R_v . The former result is consistent with star-like structures, whereas the latter can be explained considering the high sensitivity of DLS to large structures and/or to the development of shear forces in the capillary tube able to disrupt the larger aggregates. The fact that the polar core probably has an elongated structure with antiparallel placement of the zwitterionic groups is able to support the above assumption, since a break of the association at one point can cause a large reduction of the micelle's size.

Intensity vs temperature measurements at concentrations where micelles are the dominant species revealed that the micelles formed by the zwitterionic copolymers are stable at much higher temperatures than the ones made of amine-capped precursors. It seems that in the former case the high temperature resistive ionic cores stabilise the micelles (figure 10(c)).

8 STAR SHAPED POLYBUTADIENES WITH END-FUNCTIONAL GROUPS

The amine-capped star polymers provide no evidence of association in cyclohexane, whereas strong association is observed in the case of zwitterionic samples. It is evident that (a) among the different series of polymers the aggregation number decreases with increasing number of functional groups and (b) among the samples with the same number of polar groups the degree of association decreases with increasing molecular weight of the precursor polymer, due to excluded volume repulsions. These results are given schematically in figure 11.

Multifunctional samples, especially the trifunctional stars form gels even at low concentrations. This result connected with the low aggregation numbers for these samples leads to the conclusion that in very dilute solution intramolecular association dominates and by increasing concentration there is a rather sharp transition from intramolecular to intermolecular association able to produce stable gels.

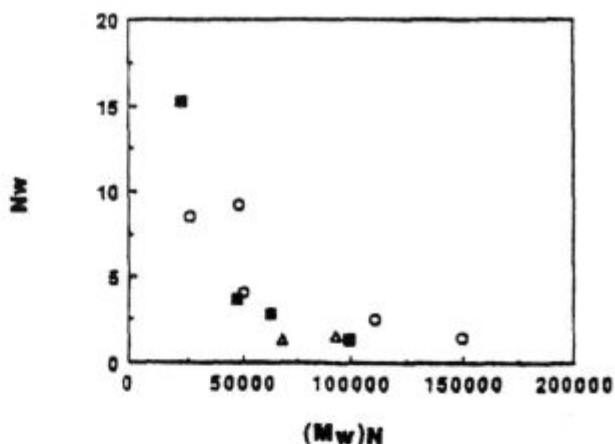


Figure 11: Weight-average aggregation number, N_w vs base molecular weight $(M_w)N$ of the star polymers: Zw-1N-3PBd (○), Zw-2N-3PBd (■), and Zw-3N-3PBd (△)

Slika 11: Utežno povprečje števila agregacije N_w v odvisnosti od molske mase $(M_w)N$ zvezdastih polimerov: Zw-1N-3PBd (○), Zw-2N-3PBd (■) in Zw-3N-3PBd (△)

The degrees of association of monofunctional stars are lower than those measured for the linear ω -functionalized PBd, meaning that the star structure prevents the association due to the steric hindrance caused by the unfunctionalized arms.

The hydrodynamic behavior of the functionalized stars was studied by DLS and viscometry³⁵. The increased values of μ_2/Γ^2 (>0.2) indicate that the aggregates produced by the zwitterionic samples are polydisperse in agreement with the MO and LALLS results. Low k_D values were observed in most cases as a consequence of the decreased second virial coefficients.

The strongly negative k_D values for the trifunctional stars indicate the existence of strong hydrodynamic interactions between macromolecular chains even though these samples have low aggregation numbers and show only small increases in R_H compared to their precursors. This behavior can be seen as evidence of intramolecular association in very dilute solutions. For the case of difunctional stars the above analysis is not straightforward. It is clear that intermolecular association cannot be ruled out.

For monofunctional samples there is no possibility of intramolecular association. The star model can be used for these samples considering that the aggregates correspond to star polymers and their precursors to the arms of these stars. Consequently, it is possible to calculate the aggregation numbers from DLS measurements, N_{DLS} . The results show that the aggregates formed from the monofunctional samples behave hydrodynamically as star polymers with functionality equal to $2N_w$. It seems that the two unfunctionalized arms anchored at the periphery of the aggregates are responsible for the overall size of micelles.

The conclusions drawn by DLS are verified by viscometry for the amine-capped polymers. Zwitterionic trifunctional samples have lower intrinsic viscosities than their precursors but the k_H values are extremely high, indicating the presence of strong hydrodynamic interactions. This behavior implies that in very dilute solutions compact structures are formed through intramolecular association. This result is in agreement with LALLS and DLS data.

Comparative examination of R_v and R_H values shows that $R_v < R_H$ for the zwitterionic polymers, meaning that the aggregates dissociate to some extent in the capillary tube, due to the shear forces applied therein. It seems that the increased steric repulsions introduced by the unfunctionalized arms lead to the formation of not so strong associates as in the case of linear polymers.

The adsorption behavior of functionalized linear and three arm star PBd was studied by ellipsometry at 20°C in a mixed solvent of cyclohexane and toluene (50% by volume)³⁶. A mixture of cyclohexane and toluene was used. In this mixture association is not detected up to the concentration of 2.0 mg/ml from DLS measurements and the dn/dc values (0.050 ml/g at 589.4 nm at 20.0°C) provide enough contrast for accurate measurements.

Various parameters of the adsorption behavior of samples are reported in **Table II**. The adsorbed amount A is increased with decreasing molecular weight for the linear samples. The longer the PBd chains adsorbed the bigger space they occupy and the stronger the repulsion between them. The ratio $\delta = D_{inter}/D_{over}$ of the interchain distance (D_{int}) over the space needed to accommodate a swollen polymer coil in a good solvent in its unperturbed state on the surface (D_{over}) is much lower than unity. This indicates that the adsorbed chains are stretched adopting a brush-like conformation.

In the case of the zwitterionic stars the adsorbed amount increases with increasing number of functionalized arms. The grafting density, defined as $\sigma = AN_A/M_w$, where A is the adsorbed amount, N_A the Avogadro number and M_w the weight average molecular weight of the

star seems to present stronger dependence on the molecular weight than the functionality of the stars. The σ values of the samples Zw-2N-3PBd30 and Zw-3N-3PBd25 are very close indicating that despite the fact that the adsorption energy is high the entropic loss involved in the attachment of the third arm when two arms are already attached may be very high.

The adsorption kinetics, studied by time-resolved ellipsometry shows two processes. In the initial stages the adsorption is diffusion controlled. By longer times the polymers must penetrate the barrier formed by the initially adsorbed chains. It was found that the star polymers penetrate this barrier faster than the linear chains, due to the different conformations adopted by the stars.

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Table II: Various adsorption parameters of ω -functionalized linear (L) and mono-(1N)-, Di-(2N)-, and tri-(3N)- ω -functionalized polybutadienes

Tabela II: Adsorpcijski parametri ω -funkcionaliziranega linearnega (L) in mono- (1N)-, di- (2N)- in tri- ω -funkcionaliziranih polibutadienov

Sample	$A_{plateau}$ (mg/m ²)	σ (chains/ nm ²)	D_{inter} (nm)	D_{over} (nm)	$\delta = D_{inter}/D_{over}$
Zw-L-PBd12	2.47±0.01	0.125	2.8	10.5	0.27
Zw-L-PBd20	2.41±0.25	0.07	3.8	14.5	0.26
Zw-L-PBd80	1.69±0.18	0.012	9.1	33.3	0.27
Zw-1N-3PBd30	1.77±0.17	0.0096	10.2	25.2	0.4
Zw-2N-3PBd30	1.86±0.06	0.0179	7.5	19.1	0.39
Zw-2N-3PBd40	1.90±0.12	0.0128	8.8	25.2	0.35
Zw-3N-3PBd25	2.14±0.18	0.0191	7.2	19.7	0.37
Zw-3N-3PBd40	2.3±0.2	0.0148	8.2	24.3	0.34

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