



BEHAVIOUR OF MODIFIED AND UNMODIFIED POLYBUTADIENES IN THE SEMIDILUTE REGIME

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Abstract—The association behaviour of polybutadiene modified with 4-phenyl-1,2,4-triazoline-3,5-dione was studied in semidilute solution through static (SLS) and dynamic light scattering (DLS). The results were compared with the unmodified polybutadiene, whose behavior in semidilute solution was also studied as function of the molecular weight. At higher concentrations a small-angle excess scattering in SLS and a slow mode motion in DLS were observed both for modified and unmodified polybutadienes suggesting the presence of large clusters. Increasing the polymer concentration, the mass fraction of the slow motion increases up to values near 1, indicating a proximity to the gel point. For polybutadienes with low and medium degrees of modification cluster formation was detected for concentrations lower than for unmodified polybutadiene. The presence of these clusters is due to intermolecular association between the polar urazole groups. The behaviour of the reduced osmotic modulus for various molecular weights of unmodified polybutadiene allowed the conclusion that its association is due to segment–segment attractive interactions. © 1997 Elsevier Science Ltd

INTRODUCTION

During the past twenty years the behavior of semidilute polymer solutions has been intensively studied. By the use of scaling [1] and renormalization group [2] theories, considerable advances in the understanding of the semidilute regime have been achieved and comprehensive reviews [3–6] on the subject are available. In the semidilute regime, due to the formation of entanglements, the solution properties are no longer influenced by the individual chain, as occurs in the dilute regime. Scaling theory predicts that the semidilute solution properties of linear chains are independent of the molecular weight. This prediction was confirmed experimentally by many studies on polystyrene in various thermodynamically good solvents [4]. However, some experimental facts cannot be explained in light of the theories mentioned above, as for example the appearance of a slow mode in the time correlation function measured by dynamic light scattering (DLS). The origin of this slow mode still constitutes a controversial point in the DLS literature. Many researchers [4, 7–10] accept that clusters are responsible for the appearance of the slow mode but the reasons of the formation of these clusters still remain unclear. It was shown entanglements play a role in cluster formation [4]. It was also verified that clusters may build up due to specific interactions between chain segments [7]. In recent years a different interpretation for the origin of the slow mode was

formulated by Wang [11] through a hydrodynamic theory: the slow mode would arise when there is a coupling of the concentration fluctuation to stress relaxation modes. This coupling in turn should occur when a difference between the densities of the polymer and of the solvent exists [12]. Experimental results obtained for polystyrene (PS) in various solvents [12–14] were well described by this theory.

Most of the work about semidilute solution properties was done on linear chains [8, 15–18] while investigations on branched structures [9, 19] are comparatively scarce. The purpose of this work was to study the semidilute solution properties of chemically modified and unmodified polybutadienes by static and dynamic light scattering. Polybutadiene was modified by reaction with 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) as reported in a previous paper [20]. The static and dynamic light scattering studies in dilute solution showed the modified polybutadiene presented behavior typical of branched structures [20]. This was a consequence of hydrogen bonding association between the polar urazole groups introduced in the polymer chain by the reaction with PTD. Once branching was detected for the modified polymer, the determination of the fraction of rings proved to be of special interest. This was performed by applying a Fourier transform infrared spectroscopic analysis of the association equilibrium between the urazole groups and it was verified that the fraction of rings in this system was very high (95–99%) [20].

EXPERIMENTAL

All polybutadiene samples were anionically synthesized with *sec*-butyl lithium as initiator and cyclohexane as

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solvent [21]. The samples showed a microstructure of *ca* 96% *cis/trans* 1,4-units and 4% 1,2-units [21]. The triazolinedione was prepared according to the literature [22]. The modification procedure of polybutadiene with triazolinedione is described elsewhere [23]. Refractive index increments of the materials were measured in tetrahydrofuran (THF) at 20°C as described previously [20].

Due to their high viscosities, the semidilute solutions for light scattering measurements could not be filtered as usual, therefore they were prepared as follows. The concentration of a dustfree solution which could still be filtered was increased by applying an oil pump vacuum. For this purpose the cuvette was covered with a membrane filter (Sartorius, teflon-filter, 1.2 μm) and placed vertically in a pointed dustfree flask, which was connected to a dustfree sintered glass filter. The concentration was determined by weight difference. In order to homogenize the solution, the cuvette was shaken. The pure solvent was treated in the same way and showed no change in the scattering intensity. Samples were prepared by this procedure in a concentration range where solutions could still be filtered. A comparison with directly filtered samples showed the same results. After dilution of solutions which displayed a slow motion, this effect disappeared.

The light scattering measurements were performed at 20°C in THF with an automatic ALV goniometer and an ALV-3000 correlator. A Spectra-Physics (model 2020) krypton ion laser ($\lambda = 647.1 \text{ nm}$) was used as a light source. Time correlation functions were measured in multiple- τ mode in the angular range from 30° to 150° in steps of 30° or 20° and by using 192 channels with a starting sample time of 1 μs .

RESULTS AND DISCUSSION

Unmodified polybutadiene

Three samples of weight-average molecular weights $M_w = 44,000$ (PB45), 92,000 (PB100) and 210,000 (PB210) g mol^{-1} were investigated. All samples showed a narrow molecular weight distribution [23]. Concentrations up to 100 g l^{-1} were studied for the three samples. Another sample of high molecular weight PB1000 ($M_w = 1,050,000 \text{ g mol}^{-1}$) could be studied only to a concentration of 40 g l^{-1} . Due to the high viscosity, dustfree solutions of higher concentrations could not be prepared.

With the exception of this high molar mass material, no angular dependence up to a concentration of about 40 g l^{-1} was found for all samples. For PB100 at about 60 g l^{-1} a weak angular dependence could be seen and at higher concentrations a very pronounced angular dependence became detectable (Fig. 1).

The results may be analyzed in terms of the osmotic modulus (equation 1), which is given by the forward scattering. This requires an extrapolation of the angular dependence of the scattering intensity to the zero scattering angle.

$$K_c/R_{\theta=0} = (1/RT)(\delta\pi/\delta c) = (1/M_w) + 2A_2c + 3A_3c^2 + \dots \quad (1)$$

This equation can be rewritten in the following dimensionless form:

$$M_w K_c/R_{\theta=0} = 1 + 2A_2 M_w c + 3g_A (A_2 M_w c)^2 \quad (2)$$

where use has been made of the fact that the third virial coefficient can be expressed in terms of A_2 as follows:

$$A_3 M_w = (A_2 M_w)^2 g_A \quad (3)$$

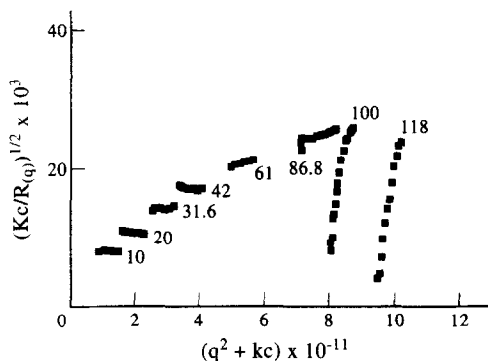


Fig. 1. Berry-plot for some high concentrations of the unmodified polybutadiene PB100. The numbers indicate the concentrations in g l^{-1} .

in which the parameter g_A is structure dependent. In the theory of A_2 one has:

$$A_2 M_w = 4\pi^{3/2} N_A (R_g^3/M) \psi(z) \quad (4)$$

in which R_g is the radius of gyration and $\psi(z)$ is the so-called coil interpenetration function [24]. This function increases with increasing interaction parameter z until it reaches a nearly constant plateau beyond $z = 0.75$ [2]. In this asymptotic region of a good solvent the coil behaves like an equivalent hard sphere; the quantity $A_2 M_w$ acquires the meaning of an inverse concentration, which is thermodynamically defined as the overlap concentration c^* . Equation (2) indicates universal behavior for a special class of polymers and suggests a plot of the reduced osmotic modulus $(M_w/RT)(\delta\pi/\delta c)$ against $X_A = A_2 M_w c = c/c^*$. In this plot all measurements of different molecular weights should form one common master curve. Figure 2 shows that this is indeed the case for all the samples as long as X_A is smaller than 3. At higher concentrations the forward scattering resulted

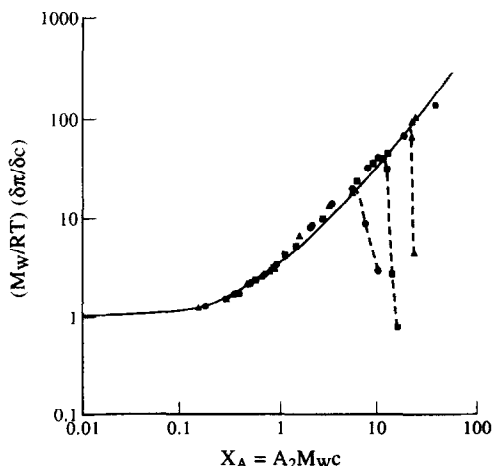


Fig. 2. Reduced osmotic modulus of polybutadiene of various molecular weights against the scaling parameter $X_A = A_2 M_w c$ (●: PB45, ■: PB100, ▲: PB210, ●: PB1000).

in a strong downturn, which was dependent on the molecular weight of the polybutadiene. This means the universal behaviour no longer exists beyond this region. The full line corresponds to the theory of Ohta and Oono [25]. The corresponding curve for polystyrene [5] was found to lie above the theoretical curve. In other words, the repulsion between the polybutadiene chains is lower than that between the PS-chains. This fact agrees with the translational diffusion behavior in dilute solution: polybutadiene was found [20] to have a lower coil interpenetration parameter ($k_{f0} = 4.3$) than polystyrene ($k_{f0} = 6.3$) [26], where k_{f0} is defined by the relationship:

$$k_{f0} = [2A_2M_w c - k_D - v]/(N_A V_h M) \quad (5)$$

here v is the partial specific volume, k_D describes the concentration dependence of the diffusion coefficient,

$$D_c = D_0(1 + k_{DC}) \quad (6)$$

and the hydrodynamic volume is $(4\pi/3)R_h^3$, where R_h is derived from D_0 by the Stokes–Einstein relationship:

$$D_0 = kT/(6\pi\eta_0 R_h) \quad (7)$$

A very interesting result can be extracted from Fig. 2. For the three samples the dashed lines of non-universal behavior begins at $X_A \sim 6$, $X_A \sim 10$, $X_A \sim 20$, respectively. These values of X_A correspond in all cases to about the same concentration of $c = 75 \text{ g l}^{-1}$, i.e. the concentration at which association first became detectable is approximately the same for all molecular weights. For liquid crystalline polymers in semidilute solution an independence of the incipient association from the chain molecular weight was also reported [7]. These unexpected findings give strong evidence that the segment concentration plays a decisive role in the anomalous behavior of the reduced osmotic modulus of polybutadiene and not the overlap concentration c^* . In other words, the increase of the molar mass is due to segment–segment association rather than by entanglements. Figure 3 shows the inverse of the apparent molecular weight plotted against the concentration. One can clearly see diverse dependences in the dilute regime for all four samples of different molecular weights. In the semidilute regime the curves tend to converge to a common behavior, since in this regime the solution properties become independent of the chain length [1]. Beyond $c = 75 \text{ g l}^{-1}$ a downturn is observed for all molecular weights meaning again that specific interactions between chain segments are active.

The downturn of the reduced osmotic modulus and the onset of the small angle excess scattering are accompanied by the appearance of a slow motion in the dynamic light scattering. Up to concentrations of 40 g l^{-1} , where there is no angular dependence in the static light scattering, only a rapid motion can be seen. Above $c = 75 \text{ g l}^{-1}$ a distinct slow motion is present for all three samples. Figure 4 shows as a typical example the behavior of the sample PB100 as a function of concentration. An incipient slow relaxation is detectable at $c = 60 \text{ g l}^{-1}$ but disappears at higher angles.

The inflection points of the curves in Fig. 4 represent the mean relaxation times, their extrapol-

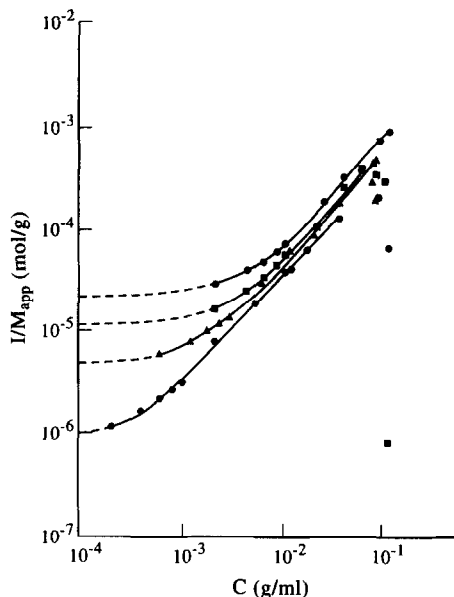


Fig. 3. Inverse of the apparent molecular weight against the concentration of polybutadiene. Symbols as in Fig. 2.

ation to $q^2 = 0$ was also carried out. In order to separate both motions from each other, use of the Laplace inversion program CONTIN [27] was made allowing the obtention of the diffusion coefficients of the fast and the slow modes. Unfortunately, the distribution of the relaxation times was not accessible. Angular dependence was not verified for the diffusion coefficient of the fast mode but it was detected for the slow mode. This is shown for a representative sample in Fig. 5. This fact indicates that the slow mode for polybutadiene in THF is certainly not due to a dynamical coupling between the concentration fluctuation and the stress relaxation mode. According to this coupling mechanism [14], the slow mode should show angular dependence at high scattering vectors while the fast mode should be angular dependent. Furthermore, the coupling parameter β [13] for the system polybutadiene/THF is negligible, since the difference in densities between the polymer and the solvent is very small. (The density of the polybutadiene samples depends on the microstructure and lies in the range 0.89–0.95; the density of THF equals 0.8892 at 20°C [28].)

At constant molecular weight the diffusion coefficient of the slow motion, D_{slow} , becomes smaller with increasing concentration. As expected, at similar concentrations D_{slow} is smaller for higher molecular weights (Table 1).

The height of the plateau of the time correlation function is proportional to the weighted mass fraction of the slow motion. Extrapolating the plateau values to the zero scattering vector, one obtains the mass fraction of the slow motion. Figure 6 shows that the mass fraction of the slow motion increases with the concentration.

One may try to describe also the reduced diffusion coefficient D_c/D_0 in terms of c/c^* , where various definitions of c^* can be used. We applied four scaling parameters c/c^* , i.e. $A_2M_w c$, $c[\eta]$, $k_{f0}c$ and k_{DC} , where

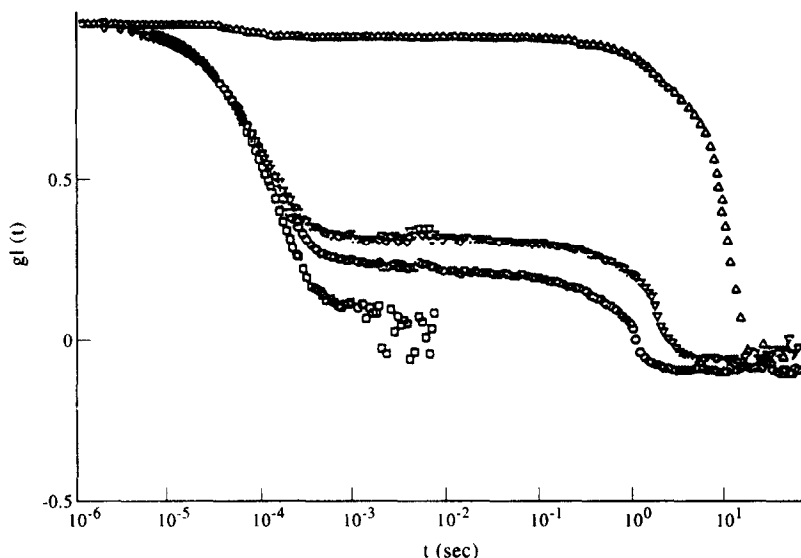


Fig. 4. Time correlation functions against time for the unmodified PB100 at an angle of 30° as a function of the concentration (\triangle : 100 g l^{-1} , ∇ : 86.8 g l^{-1} , \bullet : 61.3 g l^{-1} , \square : 40 g l^{-1}).

$A_2M_w c$ is a static quantity, whereas the three others are hydrodynamically defined. If D_c/D_o is plotted against $X_A = A_2M_w c$ or $c[\eta]$, one observes agreement of the results for polybutadiene with the theoretical curve for hard spheres [29]. Polybutadiene chains are, however, known not to be hard spheres, thus this agreement can be interpreted only as a mere coincidence. If D_c/D_o is plotted against k_{fc} and k_{DC} , different results are obtained. An agreement with the theoretical curve for hard spheres exists only for $k_{fc} < 10$. If k_{DC} is chosen as the scaling parameter, an agreement with hard spheres is no longer observed [23]. The experimental points lie near the curve of flexible chains [30] (Fig. 7), but agree with it only for $k_{DC} < 0.4$.

The modified polybutadiene

Three samples were studied in the semidilute regime, namely PB1004, PB1009 and PB10020. The

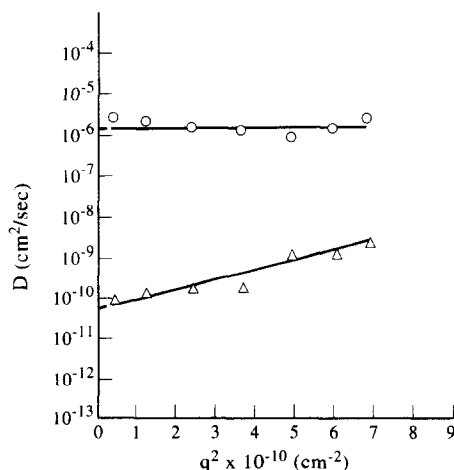


Fig. 5. Angular dependence of the diffusion coefficients of the fast ($\circ = D_{\text{coop}}$) and of the slow ($\triangle = D_{\text{slow}}$) modes for PB45 at the concentration $c = 120 \text{ g l}^{-1}$.

designations of these samples mean the starting polymer PB100 with degrees of modification equal to 4, 9 and 20 mol%, respectively. A Berry plot [i.e. $(K_c/R_\theta)^{1/2}$ against $q^2 + kc$] for PB1009 is represented in Fig. 8. No angular dependence can be seen at concentrations smaller than 20 g l^{-1} , which is also the case for the unmodified polybutadiene PB100. An increase of the scattering intensity at low angles became noticeable at concentration $c = 30 \text{ g l}^{-1}$. Beyond $c = 40 \text{ g l}^{-1}$ an angular dependence is clearly detectable, whereas for the unmodified PB100 this happens only for concentrations higher than $c = 87 \text{ g l}^{-1}$.

The results may also be analysed in terms of the osmotic modulus as shown in Fig. 9. Up to $X_A \sim 3$ all three samples with degrees of modification of 4, 9 and 20 mol% follow behavior of the unmodified polymer, which in turn agrees with the theoretical one. For PB1009 at $X_A = 4$ a transition is detectable and corresponds to a concentration of $C = 30.6 \text{ g l}^{-1}$. If only the small angles are considered for the extrapolation, the osmotic modulus decreases. On the other hand, performing the extrapolation only with the large angle data, the osmotic modulus continues to follow the dilute regime curve. A similar transition seems to be present for PB1004, but now at $X_A = 5$ ($c = 40 \text{ g l}^{-1}$). In the semidilute regime both samples

Table 1. Diffusion coefficients (in $\text{cm}^2 \text{ s}^{-1}$) of the fast (D_{coop}) and of the slow (D_{slow}) modes for various concentrations (in g l^{-1}). All D_{coop} and D_{slow} were obtained by extrapolation to zero angle with the exception of D_{slow} at $c = 61.3 \text{ g l}^{-1}$ which corresponds to $\theta = 30^\circ$

Sample	Concentration	D_{coop}	D_{slow}
PB45	120.0	2.3×10^{-6}	8.0×10^{-11}
PB45	197.0	3.5×10^{-6}	9.0×10^{-12}
PB100	61.3	1.6×10^{-6}	3.9×10^{-10}
PB100	86.8	1.8×10^{-6}	1.1×10^{-10}
PB100	100.0	2.2×10^{-6}	3.0×10^{-11}
PB210	77.0	2.1×10^{-6}	9.0×10^{-12}
PB210	84.0	2.3×10^{-6}	1.0×10^{-12}

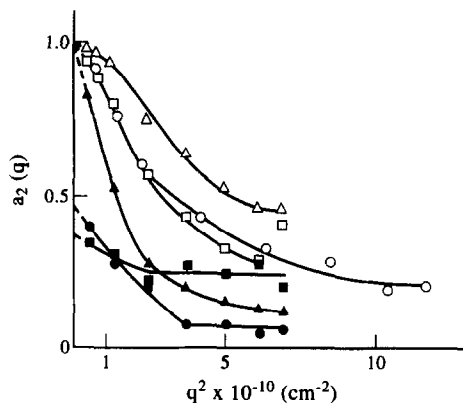


Fig. 6. Mass fraction of the slow motion $a_2(q)$ as a function of the scattering vector q^2 for PB45, PB100 and PB210 (○ PB210 $c = 84 \text{ g l}^{-1}$, ● PB210 $c = 77 \text{ g l}^{-1}$, □ PB100 $c = 100 \text{ g l}^{-1}$, ■ PB100 $c = 86.8 \text{ g l}^{-1}$, △ PB45 $c = 197 \text{ g l}^{-1}$, ▲ PB45 $c = 120 \text{ g l}^{-1}$).

follow the same curve, which appears shifted by a factor of 2 in comparison to the curve of PB10020. This indicates that at least a dimerization for the samples PB1004 and PB1009 occurs in the semidilute regime. This doubled molecular weight is actually an apparent molecular weight, since interactions are also present between the clusters. Analogously to the dilute regime, the true molecular weight would be obtained only through extrapolation to the zero concentration. For PB10020, the sample with the highest degree of modification, a dimer is present already at infinite dilution. Only intramolecular association seems to be effective up to the semidilute regime. This conclusion is supported by the fact that this sample forms a line which lies above the theoretical curve for flexible linear chains.

Furthermore, the sample PB10020 shows excess scattering at small angles at concentrations above 85 g l^{-1} ($X_A = 15$) and simultaneously the typical downturn in the osmotic modulus occurs. At $c = 42 \text{ g l}^{-1}$ there is no angular dependence and only one point was drawn in Fig. 9. When the concentration is increased, the angular dependence

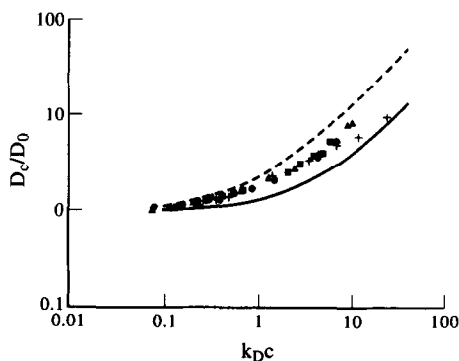


Fig. 7. Reduced diffusion coefficient D_c/D_0 against the scaling parameter k_{DC} (+: PB1000, ▲: PB210, ●: PB100, ■: PB45, --: flexible chains, —: hard spheres).

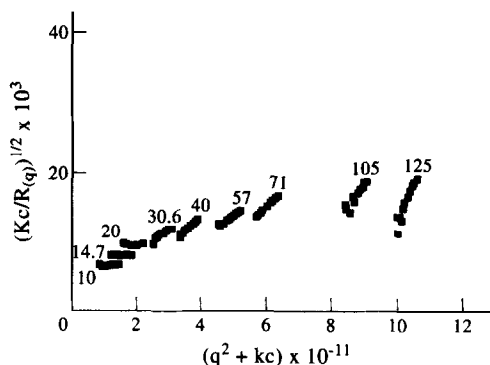


Fig. 8. Berry plot for some higher concentrations of the modified sample PB1009. The numbers indicate the concentrations in g l^{-1} .

becomes more accentuated. At $c = 106 \text{ g l}^{-1}$ ($X_A = 20$) the curve no longer approaches a plateau at large q and only one extrapolation to $q^2 = 0$ could be performed, only one point could be drawn. Such behavior was also observed for the unmodified PB100.

Figure 10 shows time correlation functions for PB1009 at various concentrations and the angle $\theta = 30^\circ$. The plateau heights increase, if the concentration is increased. This means the mass fraction of the slow motion becomes higher. At concentrations larger than 40 g l^{-1} , when an angular dependence is detectable, a slow motion is clearly seen. For a concentration of 10 g l^{-1} only a rapid motion is present, which agrees with the results of the static light scattering. However, at $c = 20 \text{ g l}^{-1}$, where no angular dependence exists, surprisingly a slow motion is still present. This fact can be explained as follows. The diffusion coefficient at finite concentration D_c is given by [24]:

$$D_c = [kT/f(c)](M_w/RT)(\delta\pi/\delta c) \quad (8)$$

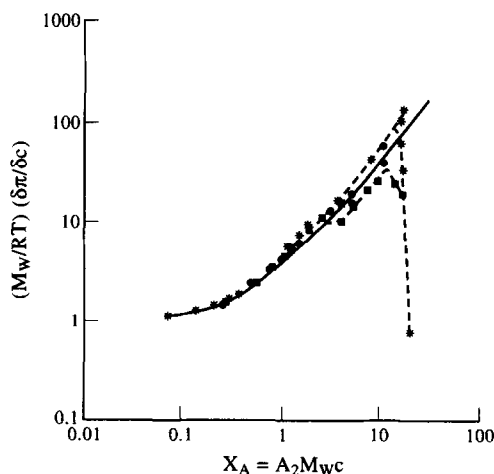


Fig. 9. Reduced osmotic modulus against the scaling parameters X_A for the modified samples PB1004, PB1009 and PB10020. The full line represents the theoretical behaviour of linear flexible chains (●: PB1004, ■: PB1009, *: PB10020).

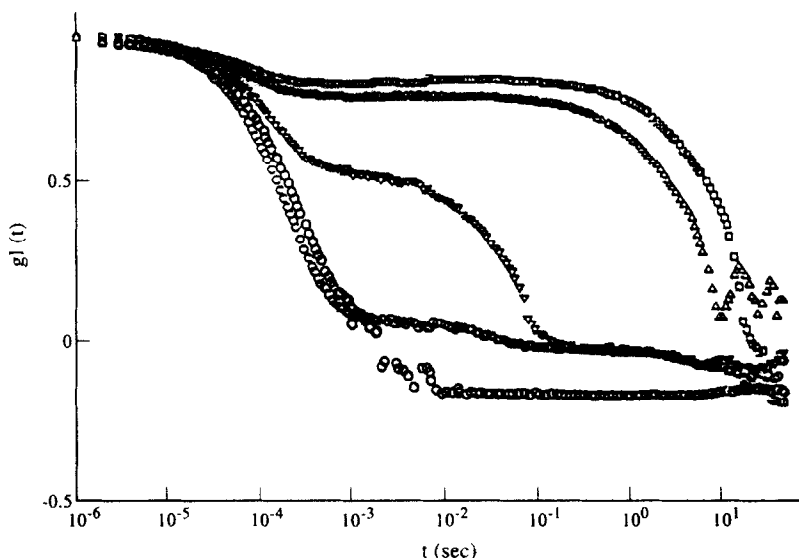


Fig. 10. Time correlation functions against the time for the modified sample PB1009 at an angle of 30° as a function of the concentration (\square : 125 g l^{-1} , \triangle : 105 g l^{-1} , ∇ : 40 g l^{-1} , \bullet : 20 g l^{-1} , \circ : 10 g l^{-1}).

The equation allows the following interpretation: in the concentration range $10\text{--}40 \text{ g l}^{-1}$ the thermodynamic interactions do not yet play a decisive role, but there seems to be a hydrodynamic effect, which is expressed by the friction coefficient $f(c)$. The sample PB1004 shows analogous behavior. Similarly for the sample PB10020 at a concentration of 42 g l^{-1} no angular dependence is present, but a slow motion already appears in the time correlation function.

The plateau heights of PB1009 and PB10020 show different angular dependences (Figs 11 and 12). The behavior of PB10020 is similar to that of the unmodified PB100 (Fig. 6). This fact indicates PB10020 possesses a mechanism of association, which is not necessarily related to the urazole groups, but is similar to the association of the unmodified polymer. At present no theory is available that would

describe the angular dependence of the mass fractions.

The concentration dependence of $(D_{\text{slow}})_{q=0}$ and $(D_{\text{coop}})_{q=0}$ for all three modified samples as well as the unmodified PB100 is shown in Fig. 13. The diffusion coefficients obtained by the method of cumulants [5, 31] are also represented. Below a concentration of 20 g l^{-1} the samples follow different curves according to different molecular weights. In the semidilute regime the samples form the same curve as expected for D_{coop} in a good solvent. The line increases with a slope of 0.76, which agrees well with that expected from the scaling theory (0.75). In this way the rapid motion can be interpreted as a cooperative diffusion between the entanglement points of the transient network. In this work D_{coop} was verified not to be angular dependent, which is to be expected, since it

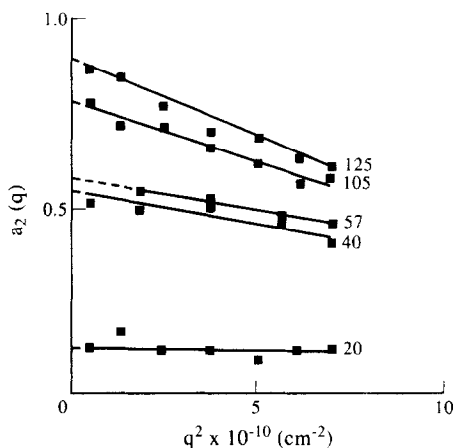


Fig. 11. Mass fraction of the slow motion $a_2(q)$ as a function of the scattering vector q^2 for various concentrations of the sample PB1009. The numbers indicate the concentrations in g l^{-1} .

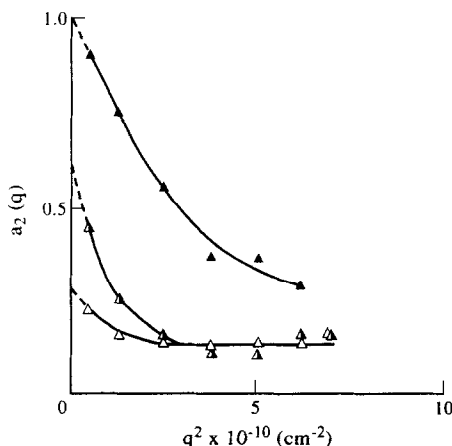


Fig. 12. Mass fraction of the slow motion $a_2(q)$ as a function of the scattering vector q^2 for various concentrations of the sample PB10020. (\blacktriangle : 106 g l^{-1} , \triangle : 85 g l^{-1} , ∇ : 42 g l^{-1}).

does not correspond to large associated particles but is related to the rather short correlation length ξ_h . (Neither should D_{coop} correspond to a coupling mechanism, since the difference in densities between THF and polybutadiene with a minor content of 1,2 units is very small.)

For D_{slow} , however, a much sharper concentration dependence was obtained than expected for reptating [1] chains. For the examined polybutadienes in THF, D_{slow} decays approximately with c^{-5} , whereas after the scaling theory D_{slow} should be proportional to $c^{-1.75}$ [1]. Therefore, the observed slow motion cannot be caused by reptation [1] of single chains. Due to the fact that a slow motion was often observed simultaneously with a low-angle excess scattering, the slow motion was assigned to the formation of large clusters [8–10].

At present the question of why such clusters are formed is still not clear. In the case of unmodified polybutadiene the results of the measurements on different chain lengths suggest that attractive interactions between the segments lead to the formation of clusters, because only beyond a certain concentration clusters were observed. In the semidilute regime the sample PB10020 differs slightly from PB100, such attractive interactions between segments of the same kind seem also to lead to cluster formation. For samples PB1004 and PB1009 cluster formation is due at first to intermolecular association between the urazole groups, i.e. at concentrations

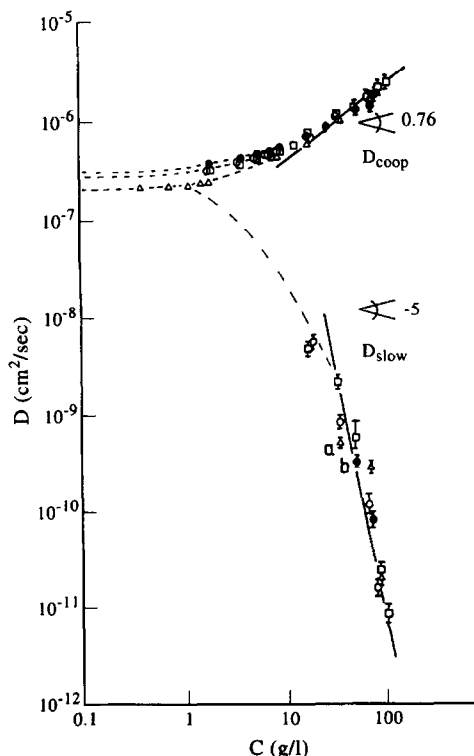


Fig. 13. Concentration dependence of D_{cum} , D_{coop} and D_{slow} for (●) PB100, (○) PB1004, (□) PB1009, (△) PB10020. Points "a" and "b" correspond to an angle of 30° . All other points were obtained by extrapolating to the zero scattering vector.

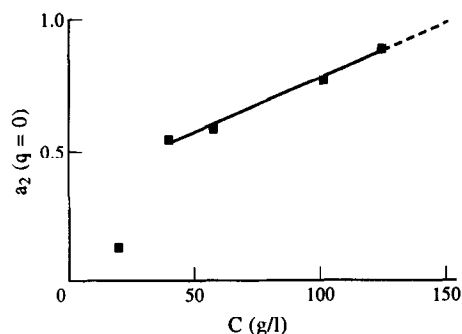


Fig. 14. Mass fraction at zero scattering vector $a_2(q=0)$ against the polymer concentration c for sample PB1009. Estimation of the gel point.

lower than for PB100. The fact, that D_{coop} for modified and unmodified samples is similar, suggests the presence of free chains besides the clusters. For higher concentrations of the modified samples, where for PB100 a slow motion is also present, attractive interactions between the segments can play, in the same way, a role in the cluster formation.

The clusters grow in size with increasing concentration and a gel point should be finally reached, where the weight-average molecular weight becomes infinite. A gel may be defined by the condition that the weighted mass fraction of clusters is 1. It was possible to estimate the gel point of the sample PB1009: the plot of the slow mode amplitude $a_2(q=0)$ against the concentration produces a straight line, and the extrapolation to mass fraction 1 furnishes a gel point of 150 g l^{-1} (Fig. 14). For samples PB100 and PB10020, the mass fraction of clusters at the highest concentrations examined ($c = 100 \text{ g l}^{-1}$) is already very high, i.e. 0.98, indicating a gel point is nearly reached. For both modified and unmodified polybutadienes the association in the semidilute regime can lead to a gel. Due to the high fraction of rings present in the modified polybutadiene [20], gel formation is shifted to higher concentrations.

CONCLUSIONS

The appearance of heterogeneities, i.e. association, can be detected in static and dynamic light scattering for all polymers, if sufficiently high concentrations are reached. Up to now the causes of such heterogeneities are not completely understood. The behavior in semidilute solution was interpreted in terms of cluster formation. Evidence of a coupling mechanism [11–14] was not found. It was verified that the association of unmodified polybutadiene is influenced by specific attractive interactions between the chain segments rather than by entanglements. For the association of the modified polybutadiene these segment–segment interactions are not excluded and, by hydrogen bonding, the urazole groups play an essential role in the behavior in the semidilute regime.

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REFERENCES

- Gennes, P.-G. de, *Scaling Concepts in Polymer Physics*. Cornell, Ithaca, New York, 1979.
- Freed, K., *Renormalization Group Theory of Macromolecules*. Wiley, New York, 1987.
- Schaefer, D. W. and Han, C. C., in *Dynamic Light Scattering*, ed. R. Pecora. Plenum Press, New York, 1985.
- Brown, W. and Nicolai, T., *Colloid Polym. Sci.*, 1990, **268**, 977.
- Burchard, W., *Makromol. Chem. Macromol. Symp.*, 1988, **18**, 1.
- Joanny, J. F. and Candau, S. F., in *Comprehensive Polymer Science*, Chap. 7, Vol. 2, ed. C. Booth and C. Price. Pergamon Press, Oxford, 1989.
- Richtering, W., Gleim, W. and Burchard, W., *Macromolecules*, 1992, **25**, 3795.
- Eisele, M. and Burchard, W., *Macromolecules*, 1984, **17**, 1636.
- Huber, K., Bantle, S., Burchard, W. and Fetters, L. J., *Macromolecules*, 1986, **19**, 1404.
- Brown, W., *Macromolecules*, 1984, **17**, 66.
- Wang, C. H., *Macromolecules*, 1992, **25**, 1524.
- Wang, C. H. and Zhang, X. Q., *Macromolecules*, 1993, **26**, 707.
- Sun, Z. and Wang, C. H., *Macromolecules*, 1994, **27**, 5667.
- Wang, C. H. and Zhang, X. Q., *Macromolecules*, 1995, **28**, 2288.
- Koberstein, J. T., Picot, C. and Benoit, H., *Polymer*, 1985, **26**, 673.
- Brown, W. and Mortensen, K., *Macromolecules*, 1988, **21**, 420.
- Wiltzius, P., Haller, H. R., Cannel, D. S. and Schaefer, D. W., *Phys. Rev. Lett.*, 1983, **51**, 1183.
- Geissler, E., Horkay, F., Hecht, A.-M. and Burchard, W., *Eur. Polym. J.*, 1994, **30**(6), 735.
- Wachenfeld-Eisele, E. and Burchard, W., *Macromolecules*, 1989, **22**, 2496.
- Bica, C. I. D., Burchard, W. and Stadler, R., *Macromol. Chem. Phys.* 1996, **197**, 3407.
- Müller-Josten, H., Diploma Thesis. Freiburg, 1988.
- Stickler, J. C. and Pirckle, W. H., *J. Org. Chem.*, 1966, **31**, 3444.
- Bica, C. I. D., Ph.D. Thesis. Freiburg, 1991.
- Yamakawa, H., *Modern Theory of Polymer Solutions*. Harper & Row, New York, 1971.
- Ohta, T. and Oono, Y., *Phys. Lett.*, 1982, **89A**, 460.
- Huber, K., Burchard W. and Akcasu, A., *Macromolecules*, 1985, **18**, 2743.
- Provencher, S. W., *Comput. Phys. Commun.*, 1982, **27**, 213, 229.
- Stephens, H. L., in *Polymer Handbook V-I*, ed. J. Brandrup and E. H. Immergut. Wiley-Interscience, New York, 1989.
- Batchelor, G. K. J., *J. Fluid Mech.*, 1976, **52**, 45.
- Oono, Y., Baldwin, P. R. and Ohta, T., *Phys. Rev. Lett.*, 1984, **53**, 2149.
- Koppel, D. E., *J. Chem. Phys.*, 1972, **57**, 4814.