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ORIGINAL CONTRIBUTION

H. Bauer
N. Böse
P. Stern

Viscoplastic flow and shear thickening in concentrated diblock copolymer solutions

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Dr. H. Bauer (✉) · N. Böse
Physikalisch-Technische Bundesanstalt
Gruppe 3.2
Bundesallee 100
38116 Braunschweig, Germany

P. Stern
Institute of Hydrodynamics
of the Czech Academy of Science
Prague, Czech Republic

Abstract Concentrated (typically 6%) solutions of a polystyrene-polyisoprene diblock copolymer in low viscosity paraffinic solvents form a micelle system by precipitating the polystyrene blocks, whereas the polyisoprene blocks are in solution. Besides viscoplastic behavior without thixotropy, this system exhibits a pronounced shear thickening in steady-state shear flow. The micelles are stable up to shear rates of more than 10^5 s^{-1}. The properties of the solutions, especially the shear-thickening behavior, depend on the thermal history of the samples as well as on the solvent properties and are sensitive to flow field disturbances occurring in rotational viscometer devices with a profiled surface structure as commonly used to avoid wall slip in dispersed materials. The shear thickening is found to be related to the formation of a long-range ordered structure which also gives rise to the yield point. This long-range order enables aggregate flow with less energy dissipation at low shear rates. Shear-induced break-up of the aggregates appears as a shear-thickening transition which is observed in different types of flow fields.

Key words Plastic flow – shear thickening – diblock copolymer solution – rotational rheometry – micelle system

Introduction

The rheology of block polymer solutions has been the subject of numerous studies, a synopsis of which is given by [1]. Such solutions often exhibit peculiar rheology, especially when diblock copolymers are dissolved in selective solvents which dissolve only one of the polymer blocks, but precipitate the other, causing the formation of a micelle system. A great number of investigations has been carried out on styrene-butadiene diblock copolymers in various types of selective solvents. In many cases plastic flow and marked thixotropy were observed in steady shear measurements, whereas nonlinear viscoelastoplasticity was found in dynamic measurements [2–4].

With solutions of a linear diblock copolymer from polystyrene and polyisoprene in *n*-paraffinic solvents (mainly *n*-octane, *n*-undecane) not only viscoplastic flow, but also time- independent shear-thickening (dilatancy) was observed which is characterized by a pronounced transition to a high viscosity state at a threshold shear rate [5, 6]. These solutions show good shear stability, reversibility of steady shear flow curves, viscoplastic flow without thixotropy, a yield value almost independent of temperature (in a certain temperature range) and are therefore of special interest for application as viscoplastic reference liquids.

However, understanding the shear-thickening phenomenon observed in this system and knowledge of the parameters that influence this flow behavior are not satisfactory at present. Flow curve measurements with concentric cylinder rotational viscometers with a profiled cylinder surface, carried out to check for wall-slip influence, gave some unexpected results which indicate that the assumption of viscoelastic deformation of micelles being responsible for the shear-thickening behavior [6] may not be sufficient to explain the experimental results.

In this paper we report the results of an experimental investigation on the shear-thickening behavior of this polymer system which was carried out, with particular emphasis on the thermal history of the samples and the influence of the measuring geometry used for flow-curve determination including high-shear measurements up to 10^6 s^{-1}.

Experimental methods

The polymer used in our investigations is a linear diblock copolymer consisting of styrene and isoprene (SI), the latter being hydrogenated after the polymer has been formed. It is available as a commercial product (Shellvis 50, Shell Company). The average molecular weight is about 100 000 g/mol, with a narrow mass distribution as characterized by a ratio of mass average to number average of 1.04. The mass fraction of the styrene block in the polymer molecule is 37%. This polymer is dissolved at temperatures between 40° and 120 °C in a low viscosity paraffinic solvent (viscosity 1.35 mPa·s at 20 °C) mainly consisting of n-C_{11} and n-C_{12}. The polymer concentrations were varied between 3% and 8% (mass fraction). As could be seen from comparative measurements with pure n-C_{11} as a solvent, the non-uniform molecular weight of the paraffinic solvent has no influence on the rheological properties observed [5]. All samples are homogeneous and optically clear transparent gels.

Flow curves under equilibrium conditions of shear were measured with both controlled shear rate (CR) rotational viscometers (Haake CV100, CV20N, M5; Contraves Rheomat 30) and a controlled stress (CS) instrument (Bohlin CS10) using various concentric cylinder and cone-and-plate geometries.

In order to investigate the possible influence of wall slip, different concentric cylinder systems with axial grooves on the cylindrical part of the surface (profiled systems, see Table 1) and a system with rough surfaces (sand-blasted surface roughness 6 μm) were used. The bottom of the cup and the end faces of the inner cylinder were smooth. The profiled structure consists of 42 grooves of 0.3 mm depth independent of the diameter of the system. The ratio of groove width to step width is usually 6:1, but also ratios of 1:1 and 1:3 (narrow grooves) were chosen to investigate the influence of the profile structure on the flow curves. In the following "profiled system" refers to a ratio of 6:1 (unless otherwise stated) for both the inner and outer cylinder of the system that was used in most measurements. The influence of the profiled cylinder surfaces on the flow field can be taken into account by a correction to the radii R_i and R_0 of the inner and outer cylinder [7]. These corrections were determined by calibration with several Newtonian reference liquids and are listed together with the geometry dimensions of the system in Table 1. It was found that the radius correction ΔR is proportional to the radius R but independent of shear rate and viscosity. For the standard value of $\delta = R_0/R_i = 1.0847$ (DIN 53 019, ISO 3219) the radius correction is given by $\Delta R = 6.7 \cdot 10^{-3} \cdot R$ in the case of a 6:1 ratio for groove to step width.

The concept of representative values (in the first order approximation) is used to calculate shear stress τ and shear rate $\dot{\gamma}$ [8].

$$\tau = \tau_{\mathrm{rep}} = \frac{1}{2}(\tau_i + \tau_0)\ \tau; \quad \tau_0 = \frac{1+\delta^2}{2\delta^2} \cdot \tau_i \tag{1}$$

$$\dot{\gamma} = \dot{\gamma}_{\mathrm{rep}} = \omega \cdot \frac{1+\delta^2}{\delta^2 - 1} \tag{2}$$

τ_i and τ_0 are the shear stress at the inner and outer cylinder, ω is the angular velocity.

Table 1 Characterization of concentric cylinder systems with profiled surfaces. p indicates that the ratio of the groove width to the step width is 6:1
$\delta_{\mathrm{corr.}} = (R_0 + \Delta R_0)/(R_i - \Delta R_i)$

System	Surface structure R_0	R_i	R_0 mm	$\delta = R_0/R_i$	ΔR_0 mm	ΔR_i mm	$\delta_{\mathrm{corr.}}$	$\lvert\Delta\tau\rvert/\tau$ %	$\lvert\Delta\dot{\gamma}\rvert/\dot{\gamma}$ %
RM 27	p	p	24	1,085	0,19	0,19	1,103	0,2	19,3
CV 54	p	p	11	1,093	0,10	0,10	1,114	0,3	21,6
CS 88	p	p	14	1,083	0,11	0,11	1,102	0,2	21,5
CS 89	p	–	14	1,084	0,10	0	1,093	0,6	8,7
CS 90	–	p	14	1,083	0	0,12	1,093	– 0,9	10,4
CS 95	p	p(1:1)	14	1,083	0,11	0,05	1,095	0,1	8,9
CS 96	p	p(1:3)	14	1,083	0,11	0,01	1,100	0,03	2,1
CS 98	p	p	14	1,022	0,08	0,08	1,034	0,05	34,7

Even though the corrections ΔR are only of the order of 0.1 mm, their influence on the calculation of shear rate, according to Eq. (2) is significant, whereas the shear-stress correction is almost negligible. The corresponding corrections to $\dot{\gamma}$ and τ are listed in Table 1. The end-effect correction is assumed to be the same for profiled and for smooth systems, and is taken into a account by a constant value determined for each system individually with Newtonian liquids (standard value $c_L = 1.10$). This is not correct for non-Newtonian liquids, especially for viscoplastic flow near the yield point [9], but this is not essential for the purpose of this study.

Besides cone-and-plate geometries (1°, 4°, $R = 20$ mm and 0, 5°, 3°, $R = 26$ mm) a high-shear concentric cylinder system ($R = 10$ mm smooth surface) with an extremely narrow gap of 0.03 mm is used. Shear rates up to 10^6 s^{-1} are achieved in a pressure-driven capillary viscometer (HVA 6, Paar) operating with nitrogen up to 130 bar (capillary length 100 mm, diameter 0.3 mm).

Results

Influence of temperature

Samples that have been prepared at different temperatures exhibit different flow properties as shown in Fig. 1. When the polymer is dissolved at 40 °C a Herschel–Bulkley type viscoplastic flow curve is obtained, and smooth and profiled cylinder systems produce identical results. For samples that have been heated to 60 °C and above, the flow curve starts with a significantly lower viscosity followed by a sudden shear-induced transition to a high viscosity state which is observed when profiled systems are used. These measurements were performed in a controlled stress instrument. When a controlled shear viscometer is used, the transition step in the flow curve is always horizontal because of the different mode of operation of this type of instrument. When smooth systems are used, the 60 °C sample remains in the low viscosity state. Increasing the heat treatment temperature to 80 ° and 100 °C causes only little change in the results obtained with smooth systems, but flattens the shear-thickening step and moves it to lower shear rates in the case of profiled systems. When the fluid has been heated to 120 °C the flow curves measured with smooth and profiled systems again coincide. As can be seen from Fig. 2, which shows the same flow curves in the low shear-rate range, the 120 °C sample still exhibits shear-thickening behavior. This, however, is less pronounced and only appears as a change of slope in the flow curve. Also, a slight difference between measurements with smooth and profiled systems is observed in this transition range.

According to these observations three different types of samples can be defined which will be called type A, B, and C. Type A solutions are those with flow properties like the 40 °C sample (flat onset of flow curve, high viscosity, no difference between smooth and profiled systems). Type B are samples (60 °C to about 100 °C preparation temperature) which have different flow curves in smooth and profiled systems, and type C corresponds to the behaviour of the 120 °C sample as described above.

The extrapolation of the flow curve to $\dot{\gamma} = 0$ in a linear scale is considered as the yield point in this work, though there is creep flow at somewhat lower shear stresses as shown in Fig. 3. The shear-rate axis in Fig. 3 does not describe the true situation because at low shear rates only part of the sample in the annular gap undergoes shear

Fig. 1 Flow curves at 20 °C for samples (6% polymer) having undergone different heat treatment. o systems with smooth surfaces; x systems with profiled surfaces

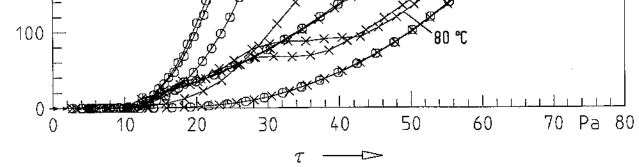
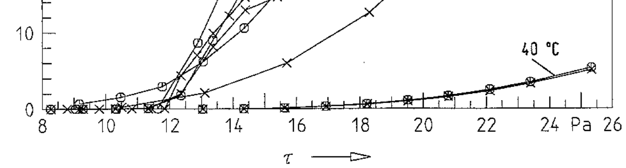


Fig. 2 Flow curves at low shear rate 20 °C for samples (6% polymer) having undergone different heat treatment. o systems with smooth surfaces x systems with profiled surfaces



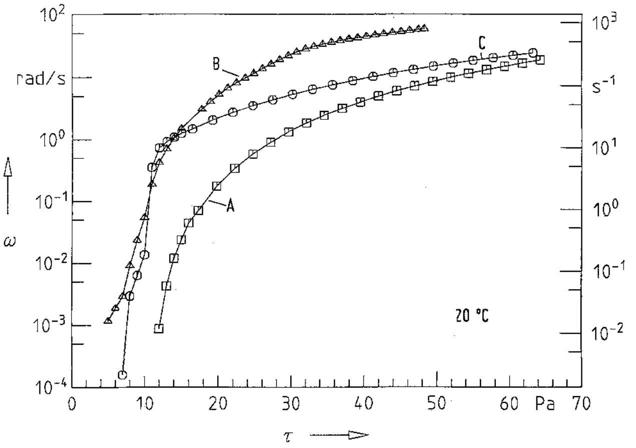


Fig. 3 Low shear measurements at 20 °C in concentric cylinder systems with smooth surfaces for three different types of samples A, B, C (6% polymer) with different preparation temperatures. Angular velocity ω as a function of shear stress τ

flow. This axis is only shown for comparison purposes. The type C sample gives the best approximation to the Bingham model in the range just above the yield point.

The transition of a type A sample to a type B can be seen from the flow curves measured at different temperatures for a sample that has been prepared at 40 °C (Fig. 4). Between 50 °C and 55 °C an irreversible change in the structure of the sample occurs. Below this transition temperature, measurements with smooth and profiled systems agree well (for clarity only measurements with smooth systems are shown in Fig. 4 except for 60 °C). Above this transition this viscosity is significantly lower and flow curves measured with profiled systems show a pronounced shear-thickening step, as can be seen from the 60 °C curve.

This change from type A to type B involves a slight increase in density of 0.04% and an increase in the thermal expansion coefficient of 0.15% as determined by measurements with pycnometers with an uncertainty of 0.01%.

The temperature dependences of flow curves measured on a sample prepared at 120 °C (type C) are shown in Fig. 5. The shear-thickening step becomes more pronounced as the temperature is increased. It is shifted to higher shear rates and is also observed in smooth systems, but at higher shear-rates than in profiled systems. Below and above the shear-thickening step the flow curves are about the same in both types of measuring geometries. At 100 °C the yield stress strongly decreases and the step in the flow curve is reduced to a slight change in the slope of the flow curve. At 120 °C the solution becomes Newtonian. From these results it can be concluded that the transition from a type B to a type C sample is associated with the thermal destruction of the micelles. This is supported by measurements with a differential scanning calorimeter (Setaram C80) which gave an endothermic peak in the specific heat capacity $c_p(T)$ curve at 110 °C. This means that only type C samples are formed from a completely dissolved state of the polymer, whereas with type A and B samples the micelle structure is directly built up during the process of dissolution.

Influence of polymer concentration

The influence of polymer concentration of type B samples is shown in Fig. 6. Up to a 3% polymer concentration no viscoplastic but only Newtonian or shear-thinning behavior is observed. Neither shear-thickening nor a difference between measurements with smooth and profiled systems

Fig. 4 Flow curves of a type A sample (preparation at 40 °C, 6% polymer) at different temperatures as measured in concentric cylinder systems (p = profiled surface)

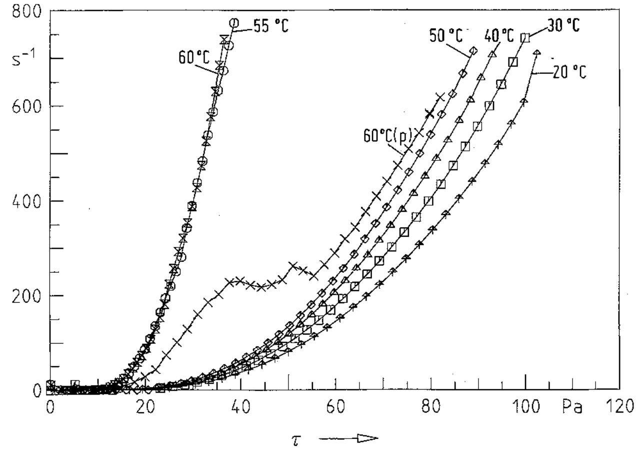
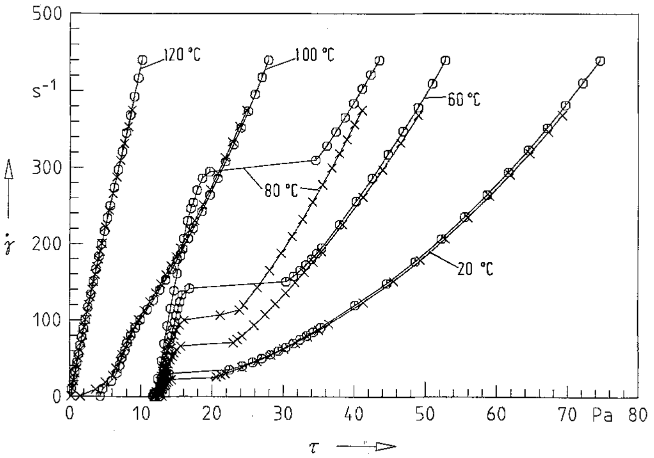


Fig. 5 Temperature dependence of the flow curve for a type C sample (preparation at 120 °C, 6% polymer). o cylinder systems with smooth surfaces; x cylinder systems with profiled surfaces



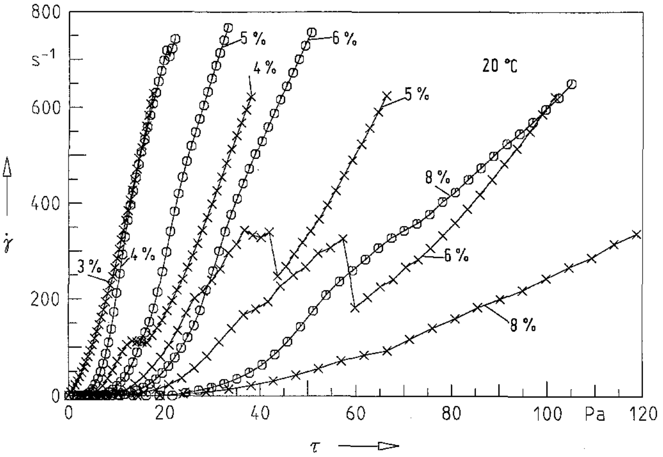


Fig. 6 Flow curves at 20 °C for type B samples of different polymer concentration. ○ cylinder systems with smooth surfaces; x cylinder systems with profiled surfaces

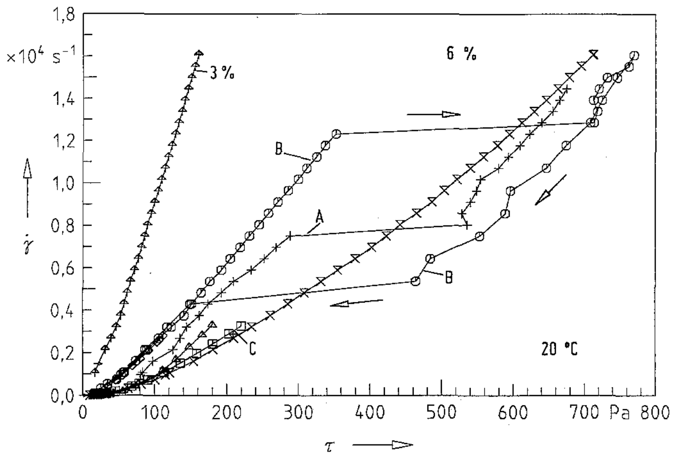


Fig. 7 High shear measurements at 20 °C for type A, B and C samples with 6% polymer and a 3% polymer solution (↑) + ○ x high shear cylinder system, sample type A, B, C; △ ◇ □ cone-and plate system (1°), sample type A, B, C

is observed. Above a 3% polymer concentration the samples exhibit a yield value which moves to higher shear stresses as the concentration is increased, and in profiled systems the shear-thickening step is also observed. With the 8% solution the shear-thickening step was not reached within the measuring range of the profiled systems.

High shear measurements

Measurements at high shear rates up to a few $10^4\,s^{-1}$ revealed that in smooth systems, type A and B samples also undergo a pronounced shear-thickening transition, but at shear rates higher by more than one order of magnitude compared with type C (Fig. 7). The flow curves are reversible, as shown for the type B sample in Fig. 7, except for the shear-thickening range where a hysteresis is observed. This hysteresis behavior is frequently associated with a sharp transition step in flow curves of this micelle system. Repeated measurements give the same results and after a 15-min exposure to a shear rate of $1.5 \cdot 10^4\,s^{-1}$, no degradation of the micelle system is observed.

Measurements with cone-and-plate geometry agree well with the results of the high-shear cylinder system except for the type A sample. However, in this case, too, the general shape of the flow curve in terms of the shear-thickening transition is supported by the cone-and-plate measurement. For comparison, a measurement on a 3% sample that exhibits no shear thickening is also shown in Fig. 7.

Higher shear rates up to $10^6\,s^{-1}$ were reached in the high-pressure capillary viscometer (Fig. 8). The results agree well with the cylinder system data. For the type B sample the shear-thickening step is also observed in the capillary flow at Reynolds numbers below 10. At high shear rates above the transition the flow curves of all three types of samples approximately coincide and can be described by a power law $\dot{\gamma} \sim \tau^n$ with a power law index $n = 1.5$.

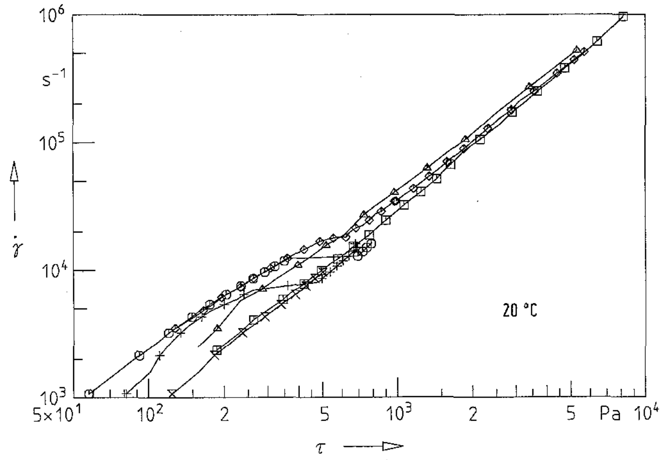


Fig. 8 High shear measurements at 20 °C in capillary flow △ ◇ □ sample type A, B, C; in couette flow + ○ x sample type A, B, C

Influence of the profiled surface structure

The influence of various profiled surface structures of the measuring system on a type B sample is shown in Fig. 9. The more the smoothness of the surface is disturbed, the more the flow curves move towards the high viscosity state that is reached with the standard (6:1) profiled system, the

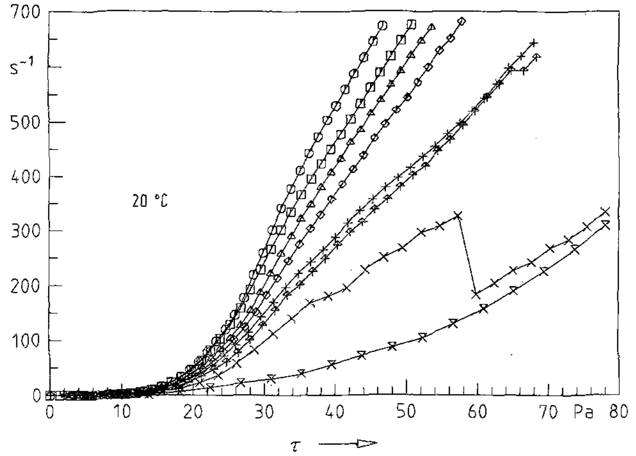


Fig. 9 Influence of the surface structure of concentric cylinder systems ($\delta = 1,08$) on the flow curve at 20 °C of a type B sample, R_0 outer cylinder, R_i inner cylinder. R_0/R_i; ○ smooth/smooth; □ rough/rough; △ profiled/smooth; ◇ profiled/profiled (1:3); + smooth/profiled; ↑ profiled/profiled (1:1); x profiled/profiled; x̄ profiled/profiled ($\delta = 1,003$)

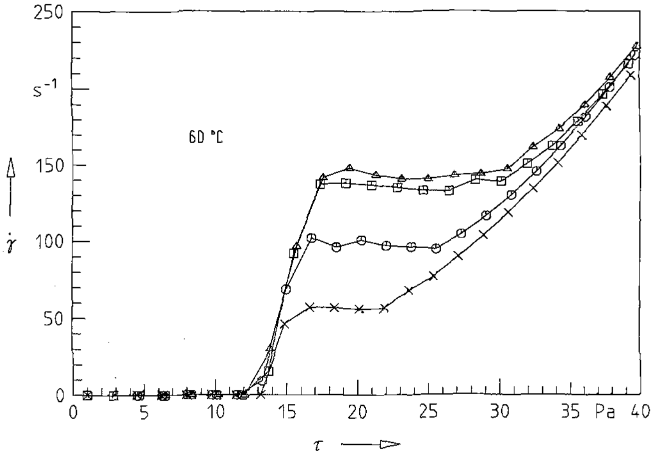


Fig. 10 Influence of the surface structure of concentric cylinder systems ($\delta = 1,08$) on the flow curve at 60 °C of a type C sample R_0/R_i; △ smooth/smooth; □ rough/rough; ○ smooth/profiled; x profiled/profiled

only one giving rise to the shear-thickening step in this range of shear rates. Considering the high shear measurements (Fig. 7), it can be expected that all these flow curves enter a shear-thickening state at higher shear rates which are, however, outside the range of these systems. The high viscosity state of the fluid (above the shear thickening) appears to be a limiting state. When a narrow gap system ($\delta = 1.003$) is applied, the high viscosity state is already observed at the onset of flow above the yield point.

For a type C sample where the steps in smooth and profiled systems are closer together, the same behavior can be seen as shown in Fig. 10. The sand-blasted surface structure has very little influence on either type B or type C samples.

Influence of solvent

The influence of solvent properties has already been reported [6]. The use of paraffins or other hydrocarbons of higher molecular mass as solvents leads to shear-thinning behavior without a yield value. If a good solvent is used for both polymer blocks, Newtonian behavior is observed. Improving the solvent quality by adding cyclohexane for example (up to 30%) to the paraffinic solvent does not generally change the shear-thickening behavior described above, but only lowers the temperature for the transition from type A to type B and from type B to type C.

From the observation that with increasing temperature of measurement the shear-thickening step is shifted to a higher shear rate, it has been concluded [6] that this is due to the change of solvent viscosity. In order to influence the flow properties of the micelle system by modifying the solvent viscosity, we added 1% of polyisobutylen (PIB) (Oppanol B50, $M_w \approx 5.10^4$ g/mol) which has about half the chain length of the isoprene block in the copolymer. The PIB dissolves in the *n*-paraffin solvent. In this case samples of type B were never observed. If the copolymer is dissolved in the *n*-paraffin + 1% PIB solvent, a direct transition from type A to type C is observed after heat treatment between 60° and 80 °C. Besides this, the addition of PIB causes a reduction of the yield stress. If the polymer is first dissolved and the 1% of PIB is added afterwards, a direct transition from type B to type C is achieved without heating the sample, as shown in Fig. 11. In this case the solvent was a mixture of *n*-paraffin with 10% cyclohexane.

Stability

The rheological properties of the polymer solutions do not change at room temperature over a long period of time. After 6 months of storage, agreement was within 2%, which is also the repeatability of the measurements. However, for type C samples the micelle system is not in thermodynamic equilibrium. After storage at 60 °C, which is well below the temperature of transition from B to type C, the flow properties change towards that of the type B, which means that the shear-thickening transition becomes more pronounced and the difference between flow curves measured in smooth and profiled systems increases

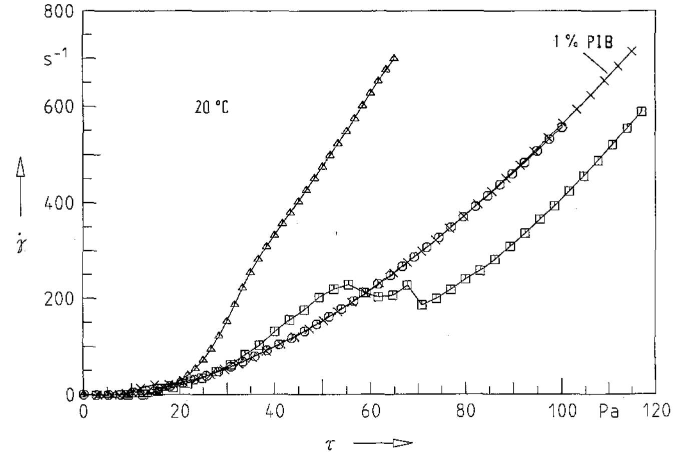


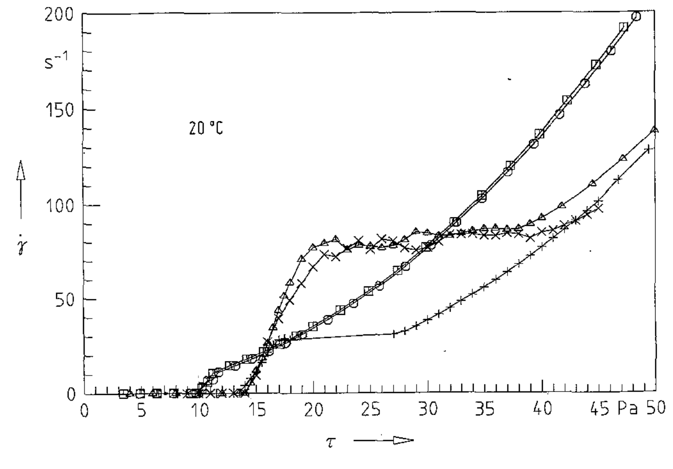
Fig. 11 Influence of 1% polyisobutylene (PIB) on the flow curves of a type B sample at 20°. △ □ without PIB, smooth (△) and profiled (□) system; x ○with 1% PIB, smooth (x) and profiled (○) system

(Fig. 12). The same effect is obtained by slowly cooling a sample to room temperature after preparation, i.e., cooling within 50 h instead of the usual 2 h. If a solvent of higher solvent power is used (*n*-octane/20% cyclohexane), a similar change is observed at room temperature.

Influence of measuring geometry

The observation of the shear-thickening step is not the result of a particular measuring geometry. It is observed in concentric cylinder, cone-and-plate (see Fig. 12), parallel-plate geometry as well as in capillary flow (see Fig. 8).

Fig. 12 Flow curves at 20 °C for a type C sample before and after a 3-month storage at 60 °C. □ ○ fresh samples; △ + x after 3 months; □ △ smooth cylinder system; ○ + profiled cylinder system; x cone and plate system



Besides this, cone-and-plate and parallel-plate systems with rough surfaces were produced by coating the systems with a tape of irregular structure with a roughness similar to the profiled geometry. With such systems no quantitative measurements could be performed but it was possible to show the existence of the shear-thickening step of type B samples in this geometry.

Microstructure

In order to gain information about the microstructure of the micelle system, wide-angle laser-light-scattering measurements were carried out with a modified photogonio-diffusometer (model 42000, Sofica). The scattering intensities were measured with a polarized incident beam of $\lambda_0 = 632.8$ nm at 11 angles from 30 to 150 degrees. The results were treated using the Zimm method, corrections for the scattering volume and the refractive index being taken into account. Table 2 shows the results for the determination of the mass average of the molecular weight M_w and the radius of gyration $\langle R_G \rangle_z$ assuming spherical geometry of the micelles.

It should be pointed out that all three samples were prepared separately by dissolving the copolymer at 40, 60, and 120 °C, respectively.

In order to carry out these light-scattering experiments the samples had to be diluted to concentrations of less than 10^{-4} g/ml. It cannot be excluded that a change in the micelle structure and size takes place due to the dilution. There are, however, indications that this may not occur since samples that were prepared at a high concentration and diluted after the micelle system had formed show results in light scattering and in rheological measurement that differ from those for samples that were directly dissolved in a low concentration.

Normal stress

Measurements of the first normal stress difference N_1 were performed with 2 and 4 degree cone-and-plate systems. For type B samples N_1 values of about 150 Pa were observed independent of shear rate, whereas for type

Table 2 Mass average M_w and radius of gyration for micelles in different samples as determined from wide-angle light-scattering measurements

Sample type	M_w g/mol	$\langle R_G \rangle_z$ nm
A	$23 \cdot 10^6$	71
B	$25 \cdot 10^6$	138
C	$7 \cdot 10^6$	99

A and type C samples the first normal stress difference increases with shear rate, but at a lower level of N_1 values (10Pa to 30Pa), as shown in Fig. 13. The shear-thickening transition does not cause a significant change in the first normal stress difference. This measurement was performed with a different solvent (*n*-octane with 20% cyclohexane) because it was possible to obtain shear thickening with a cone-and-plate system (smooth surface) at room temperature.

Discussion

According to the results of extensive studies on similar block polymers [1–4] the solutions investigated here can be considered to consist of micelles with a closed packed fairly rigid core of polystyrene (PS) surrounded by cilia of polyisoprene (PI) as shown schematically in Fig. 14 where the PS block chains are assumed to be segregated into spheres. Micelle formation is also found in dilute solutions [1], but only when the polymer concentration exceeds a limiting value is a high-order structure developed. As shown by small-angle x-ray scattering, the micelles are then arranged in a regular three-dimensional macrolattice [10–12] which was found to be essential for the existence of plasticity in such systems [10, 12]. Long-range order and plasticity are destroyed when the temperature is raised above a threshold value. In such a disordered state, the micelles still exists but will be destroyed by a further temperature increase, giving rise to Newtonian flow behavior. Our measurements agree with these results, the minimum polymer concentration for the formation of long-range order being about 4% at temperatures below 90 °C. Above 90 °C the long-range starts to break down and at 110 °C, as indicated by the endo-thermic peak in the c_P(T) curve, the micelles are dissolved.

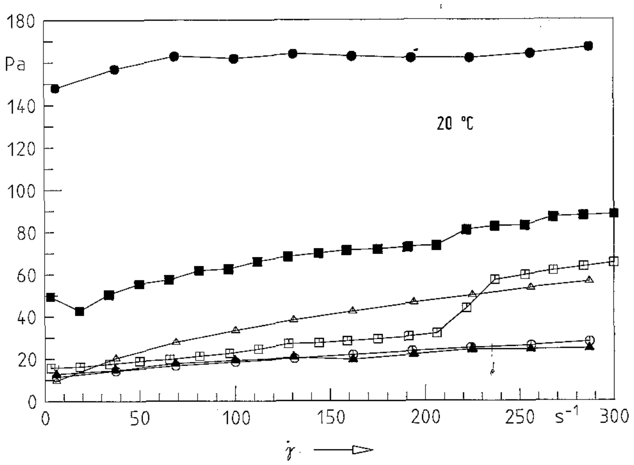


Fig. 13 Shear stress (○ △ □) and first normal stress difference N_1(●▲■) for different samples with 6% polymer. △ ▲ type B; ○ ● typce C; □ ■ type B, *n*-octane/20% cyclohexane

Fig. 14 Schematic diagram of micelles formed in solutions of a diblock copolymer in selective solvents according to [1]. PS core of polystyrene and PI cilia of polyisoprene

Shear thickening is observed in very different systems such as dilute surfactant solutions [13, 14] or concentrated dispersions [15–17] and is explained by the formation or destruction of aggregates. On other block polymer solutions or viscoplastic materials such behavior has not so far been observed. It should be pointed out that the existence of a shear-thickening transition reported here is not associated with wall slip. This was proved by the use of profiled systems, different geometries, and also by measurements in concentric cylinder systems with different gap widths.

Considering the temperature dependence of the flow curves shown in Fig. 5, it is evident that the usual viscosity-temperature behavior is found above the shear-thickening step. The differential viscosity (slope of the flow curves) just above the step fits well to an exponential temperature dependence, including the measurement at 100 °C where the step has already disappeared but viscoplastic behavior is still observed. This is supported by the concentration dependence shown in Fig. 6. The slope of the 3% curve fits to the slope for higher concentrations only above the shear-thickening step. There is clear evidence that the shear-thickening effect is associated with the existence of a long-range order, since samples without a macrolattice (no yield point) do not show this behavior. Looking at the shear-thickening step from this aspect it must be concluded that only above the step is the regular flow and energy dissipation mechanism effective, whereas below the transition the microstructure of the micellar network makes shear flow possible with less energy dissipation.

In principle, this situation is similar to that where shear-thickening effects were observed at concentrated dispersions and were explained by the formation of a shear-induced superstructure at low shear rates and a breakdown of the long-range order at higher shear rates, causing an increase in viscosity [16, 17].

In our case the long-range order already exists at rest and it must be assumed that low shear rates the rotation of the micelles in the field of shear flow is blocked by a structural arrangement, thus causing ordered layers of micelles to slip. Only when the difference between the shear stresses acting upon opposite sides of a micelle reaches a certain threshold value are the layers broken up, enabling the micelles to rotate and thus causing additional energy dissipation. With increasing temperature the shear rate necessary to produce this stress increases because of the decrease of matrix viscosity. On the other hand, the addition of 1% PIB causes an increase in the matrix viscosity, thus lowering the threshold shear rate for the destruction of the slip-layer aggregates.

The influence of the profiled surface structure of the cylinder systems can in many cases be taken into account quite well by a correction to the radii. This has been proved not only with Newtonian liquids but also with shear-thinning polymer solutions (polyacrylamide in water) and viscoplastic materials such as chocolate. However, this global correction method of introducing an increased effective gap width does not take into account that the flow field is distorted by the profiled structure. This distortion causes, for example, a reduction of the critical value for the angular velocity at which Taylor vortices are formed. In the case of a low-viscosity (5 mPa·s) Newtonian oil this value was found to be 28 rad/s in a profiled system compared with 63 rad/s calculated and measured in the corresponding system with a smooth surface. However, during the measurements reported here no such deviations from laminar flow occurred.

When profiled systems are used to measure diluted aqueous surfactant solutions (tallow-(tris-hydroxiethyl)-ammonium acetate/sodiumsalicylate mixtures, mass fraction $5 \cdot 10^{-3}$), the shear-thickening transition which is known to occur due to a shear-induced formation of aggregates is found at lower shear rates, and also a greater viscosity increase than with smooth systems is observed. In our copolymer system (which is concentrated instead of highly diluted) the mechanism responsible for the shear thickening is different, but the common feature is the formation and destruction of aggregates. These structural arrangements are sensitive to irregularities in the flow field produced by the structured surface of the measuring system, whereas materials without ordered structures are not affected by these disturbances. We therefore conclude that the distortions in the flow field of profiled systems favor the breakdown of micelle aggregates, thus leading to a shear thickening at lower shear rates. It is evident that the smaller the gap width, the greater the distortion.

In principle the three types of samples, A, B, and C, exhibit flow behavior in that for each type a yield value and a shear-thickening transition are observed. The essential differences are found in the shear rate at which the shear thickening occurs and in the shape of the flow curve at low shear rates. Above the shear thickening, the flow curves are approximately the same.

From the light-scattering experiments information on the average size and mass of the micelles is obtained, but this is not sufficient to correlate the details in the rheological behavior of the different types of samples to the microstructure of the micelle system. Since the shear thickening can be explained by shear-induced breakdown of micelle aggregates still existing above the yield point, the differences in the flow properties of the three types of samples are assumed to be due to differences in the ordered network structure. From the observation that type A samples exhibit a higher yield value than type B and C and that shear thickening cannot be induced by flow-field inhomogeneities (profiled systems), it can be concluded that a more rigid network is formed in this case. It can also be assumed that the degree of long-range order is less for type A samples since the micelles are directly formed during the solution process, whereas with type C samples micellization starts from the completely dissolved state of the macromolecules. The transition from type A to type B can be associated with the formation of a micelle network of higher order. It is possible that a change of shape also takes place, but no destruction and reformation of micelles, since the average mass remains constant. The higher degree of order leads to a reduction of the yield stress but gives rise to a more distinct onset of flow with lower viscosity. Type C samples differ from type B mainly in the stability of the micelle aggregates which are destroyed at low shear rates. This must be attributed to the difference in the mass and size of the micelles. The equilibrium state is that of a type B sample as indicated by the investigations on thermal and long-term stability.

The results of the normal stress measurements show that the shear thickening is not caused by changes in the viscoelastic properties. The assumption made earlier [5, 6] that viscoelastic deformations of the micelles are associated with their rotation in the field of shear flow cannot therefore apply to the shear thickening observed in this system.

Conclusion

The pronounced shear thickening observed in the concentrated polystyrene-polyisoprene copolymer solutions investigated in this work is associated with the existence of viscoplastic behavior due to the formation of a three-dimensional macrolattice of micelles.

When the shear stress exceeds the yield value, the long-range order of the network is only partially destroyed, and aggregates of micelles still exist at low shear rates. It is assumed that the rotation of micelles in the field of shear flow is blocked by such structural arrangements, thus causing the ordered layers of micelles to slip. These aggregates are destroyed at higher shear rates or by irregularities in the flow field caused by profiled surfaces of the measuring system, thus giving rise to a shear-thickening step in the flow curve. It is assumed that depending on the preparation temperature, micelle networks with different degrees of long-range order are formed.

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