Ultrasonic absorption and shear viscosity measurements for solutions of polybutadiene and polybutadiene-*block*-polystyrene copolymers

I. Alig, F. Stieber and S. Wartewig
Technical University 'Carl Schorlemmer' Leuna-Merseburg, Department of Physics, DDR-4200 Merseburg, GDR

and A. D. Bakhramov and Yu. S. Manučarov
Leningrad State University, Scientific Institute of Physics, Department of Molecular Physics, Leningrad, USSR

Ultrasonic measurements are reported on polybutadiene and polybutadiene-*block*-polystyrene copolymers in toluene. The ultrasonic absorption spectrum of polybutadiene can be described by the equation $\delta\alpha/f^2 \sim f^{-n}$ with the exponent $n = 1/3$. The comparison of the measured dynamic shear viscosity with effective viscosity η_{eff} shows that the ultrasonic absorption cannot simply be explained by contributions of the normal-mode relaxation. For the copolymers we can conclude from dynamic shear viscosity measurements that viscoelastic contributions have only a minor effect. The ultrasonic absorption of the diblock copolymers is higher than a pure superposition of the contributions from polystyrene and polybutadiene blocks. Therefore we assume an additional contribution from the relaxation of the volume viscosity (polymer–polymer interaction and/or polymer–solvent interaction) for polybutadiene and the copolymers.

(Keywords: ultrasonic absorption; dynamic shear viscosity; polymer solution; copolymer; polybutadiene; polybutadiene-*block*-polystyrene)

INTRODUCTION

In order to elucidate the relationship between molecular behaviour and bulk properties of polymers, interest has grown in the investigation of dynamic properties of polymer solutions. Among other experimental methods, ultrasonic measurements are a practical tool for obtaining information about the molecular mobility of such polymer systems. In recent years some excellent reviews about the application of ultrasound techniques in polymer research have been given[1-3]. There have been a number of ultrasonic investigations on homopolymers but there are fewer studies of copolymer systems. Recently we reported ultrasonic investigations of statistical and graft copolymers of poly(vinyl chloride/vinyl acetate)[4,5] and poly(vinyl chloride/vinylidene chloride) copolymer solutions[6]. In this way it was possible to study the influence of the chemical structure on the chain dynamics. The results could be explained mainly by the sum of the segmental modes of the co-components. As a model for local motions we assume different single-bond motions[7,8]. The normal-mode contributions have been assumed to give only a minor effect in this region. But there are some hints of additional contributions assigned to polymer–polymer and/or polymer–solvent interactions due to changes of the solution properties by the co-component.

The polybutadiene-*block*-polystyrene copolymers (BS) used in this study can be considered as a combination of components with different chain flexibility.

A number of papers have reported studies of ultrasonic absorption in solutions of polystyrene (PS) (see refs. 1–3

and references therein). These investigations show that the major contribution to the attenuation arises from the relaxation of rotational isomeric structures. Measurements of the dynamic shear viscosity[2,9] and calculations of the normal-mode contribution indicate that these processes have only a minor effect in the low-frequency region. For the polybutadiene (PB) some results are reported by Pethrick et al.[10,11] In these investigations it has been assumed that the major contribution for linear polybutadiene arises from the normal-mode processes and conformational relaxation. For comparison with the copolymers we also investigated polybutadiene in toluene.

We feel that it is necessary to determine the dynamic shear viscosity by a separate method in order to interpret the absorption behaviour. Therefore the dynamic shear viscosities has been measured directly for the BS and PB solutions.

EXPERIMENTAL

The ultrasonic attenuation measurements were performed over a frequency range from 0.1 to 100 MHz using the statistical reverberation method[12,13] and pulse methods[4,14,15] with accuracies of 5–10% and 3–6%, respectively. The velocity was measured by using a pulse-phase method[4]. The dynamic shear viscosity has been determined by means of a torsional resonator[16,17].

The BS samples and the high molecular weight polybutadiene have been prepared by anionic polymerization and the low molecular weight

Table 1 Characteristic data of the samples

Samples	Structure	$M_n(S)$ (g mol^{-1})	$M_n(B)$ (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n
PB 9[a]	–	–	–	8600	1.50
PB 75[b]	–	–	–	75000	<1.25
BS 25[b]	AB	75000	25000	100000	<1.25
BS 75[b]	AB	25000	75000	100000	<1.25

[a] Microstructure determined by n.m.r.: 71% 1,2; 32% *cis*; 68% *trans*
[b] Microstructure of the PB 75 and the butadiene blocks: $\approx$ 50% 1,2; $\approx$ 40% *cis*; $\approx$ 60% *trans*

polybutadiene by radical polymerization. The characteristics of the samples are summarized in *Table 1*.

RESULTS AND DISCUSSION

The excess absorption $\delta\alpha = \alpha - \phi_s\alpha_s$ was determined as a function of frequency and temperature for the PB and BS solutions in toluene, where α is the absorption coefficient of the solution, α_s the absorption coefficient of the solvent and ϕ_s the volume fraction of the solvent. In order to be able to compare the absorption to the shear viscosity data we prefer in some cases the effective viscosity η_{eff}, which is connected with the absorption coefficient by the following equation:

$$\frac{\alpha}{f^2} = \frac{8\pi^2}{3\rho v^3}\eta_{eff} = \frac{8\pi^2}{3\rho v^3}(\eta_s' + \tfrac{3}{4}\eta_v')$$

where η_s' and η_v' include relaxational effects of shear and volume viscosity. In an analogy to the excess attenuation one can define

$$\delta\eta_{eff} = \eta_{eff} - \phi_s\eta_{eff,s}$$

where η_{eff} and $\eta_{eff,s}$ are the effective viscosities of the solution and of the solvent.

Polybutadiene

The effective viscosity, the dynamic shear and the static shear viscosities of 10% solutions of PB 9 and PB 75 are shown in *Figure 1*. The broad relaxation spectrum of the effective viscosity $\delta\eta_{eff}$ of PB solution can be described by $\delta\eta_{eff} \sim f^{-n}$ with $n = 1/3$. For frequencies below 1 MHz a plateau is obvious. This type of frequency dependence corresponds qualitatively to that predicted by the Rouse–Zimm model. The dynamic shear viscosity shows the same type of frequency dependence. The plateau in the low-frequency range agrees with the static shear viscosity measured (we use for comparison in an analogy to $\delta\eta_s'$ an 'excess' static viscosity $\delta\eta_0 = \eta_0 - \phi_s\eta_{0,s}$).

The minimal relaxation frequency f_{min} of the shear viscosity spectra agrees better with the $f_{min} = 950$ kHz calculated by the Zimm theory[18] than with that calculated by the Rouse theory[19], $f_{min} = 610$ kHz. The exponent of the frequency dependence, $n \approx 1/3$, is also close to the non-draining case. This agrees with investigations of infinite-dilution viscoelastic properties of polybutadienes of higher molecular weights by the Birnboim–Schrag multiple lumped resonator[20] and indicates that the 10% solution of PB with low molecular weight ($M_w = 13\,000$) in toluene can already be considered as a dilute solution. Therefore we assume the absence of entanglements for the system investigated.

On the other hand comparison of the dynamic shear viscosity and the static viscosity data indicates that the attenuation of the longitudinal ultrasonic waves cannot only be explained by contributions of normal-mode relaxation. The ratio $\delta\eta_{eff}/\delta\eta_s'$ is about 5. Another sign that the relaxation of η_{eff} is not only connected to a Rouse–Zimm like behaviour of η_s' is that the method of reduced variables[21] does not work for η_{eff}. Furthermore, there is no considerable molecular weight dependence in the high-frequency region of the effective viscosity (see *Figure 1*), as expected from the theory for normal-mode processes and the measurements of η_0 for PB 9 and PB 75. Pethrick[10,11] assumed a combination of normal-mode and rotational isomeric processes to be responsible for the relaxation of the ultrasonic absorption between 10 and 100 MHz in the case of low molecular weight polybutadiene. We feel that the rotational isomeric processes cannot explain a broad relaxation spectrum. Furthermore one can assume low amplitudes and high frequencies for the local motions of flexible polymers like polybutadiene. Therefore we assume an additional contribution of η_v', e.g. perturbations of the solution structure. This 'excess' attenuation can be ascribed to enthalpy differences, entropy differences and/or volume differences ΔV due to perturbations of polymer–solvent and/or polymer–polymer structures.

Polybutadiene-block-polystyrene copolymers

The frequency dependence of the effective viscosity and the dynamic shear viscosity for a polybutadiene-*block*-polystyrene with 25% butadiene in solution is shown in *Figure 2* for two temperatures. For the dynamic shear viscosity we found a relaxation spectra described by an exponent $n \approx 0.3$, which indicates Zimm behaviour. Sakanishi and Tanaka[22] discussed the viscoelastic measurements of polystyrene–polybutadiene copolymers (molecular weight of about 280 000) in terms of partial draining behaviour for BSB and SBS structures and nearly non-draining behaviour for the statistical copolymer. They concluded from the correlation between the draining effects and the volume expansion that there was a more compact conformation of the SBS and BSB block copolymers compared to the statistical one. On the
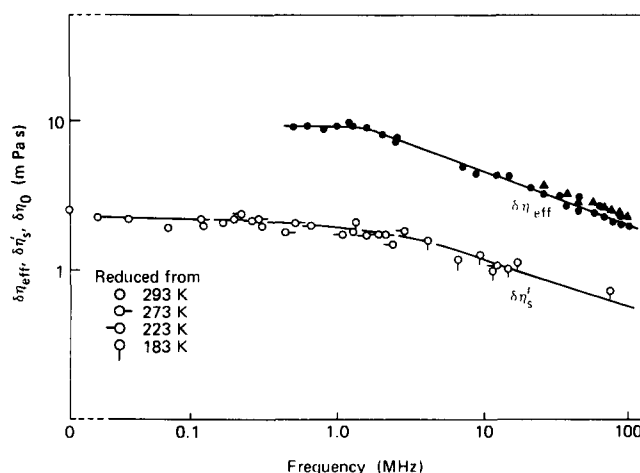

Figure 1 Frequency dependence of effective viscosity (filled symbols) and dynamic shear viscosity (open circles) of polybutadiene (●, ○, $M_n = 8600$; ▲, $M_n = 75\,000$) in toluene for $T = 293$ K (dynamic shear viscosity data reduced from temperatures indicated). Concentration 10%
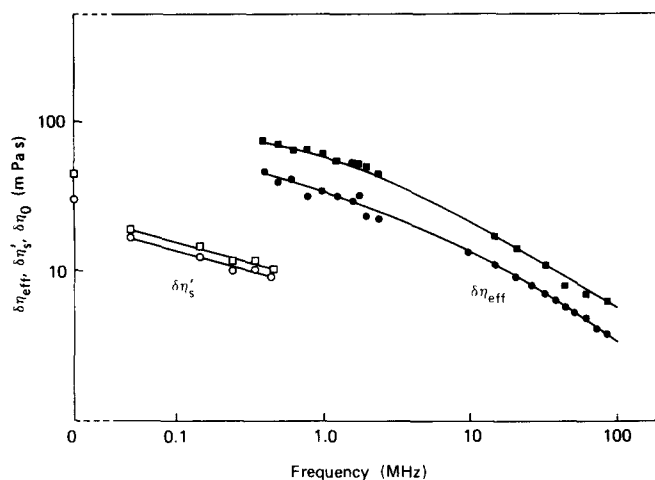
Figure 2 Frequency dependence of effective viscosity (●, ■) and dynamic shear viscosity (○, □) of polybutadiene-*block*-polystyrene (BS 25) in toluene. Concentration 10%. □, ■, 273 K; ○, ●, 293 K

Figure 3 Comparison of measured ultrasonic absorption $\delta\alpha/f^2$ of polybutadiene-*block*-polystyrene copolymer in toluene and the superposition (broken curve) of the contribution of the block components calculated from measurements of comparable homopolymers for 293 K. Concentration 10%. ●, BS 25; ○, contribution of the polybutdiene block; ——, contribution of the polystyrene block; ---, superposition

other hand, changes of the excluded-volume effect[23] or of the structure of the solution due to the co-component can also lead to deviations from the non-draining (Zimm) behaviour.

In the frequency range around 1 MHz the ratio between effective viscosity and dynamic shear viscosity is about 7 at 273 K and about 5 at 293 K, which shows that the viscoelastic contribution to the acoustic absorption has only a minor effect in the high-frequency region. The different temperature dependences of η'_s and η_{eff} indicate that another type of dissipation mechanism is mainly responsible for the contribution of the volume viscosity. From extensive investigations of polystyrene solutions[2,3] (see also references therein) one can conclude a strong contribution from rotational isomeric processes. Because of the different components of the copolymer a spectral decomposition by one or more relaxation times or a relaxation time distribution was not useful.

For comparison we have calculated the contributions of the polystyrene and polybutadiene blocks derived from homopolymers with comparable molecular weight. For the polystyrene blocks we applied the experimental values for a polystyrene solution ($M_w = 97\,000$) measured by North *et al.*[24] It seems to be possible to use these values because the relaxation strengths and relaxation times do not depend on the molecular weight for samples with molecular weights higher than about 10 000. For the polybutadiene blocks we used the values from PB 9. It is obvious that the ultrasonic absorption of the block copolymer solution cannot just be explained by a superposition of the losses in the corresponding homopolymer systems (*Figure 3*). We assume that the change in the solution structure can lead to additional relaxational processes. It is well known that copolymer solutions can have complicated structures[25,26]. Accordingly, it is possible that inter- and intramolecular polymer–polymer structures and/or polymer–solvent structures are pressure- or temperature-dependent and thus lead to an additional thermal or volume relaxation. It should be noted that ultrasonic absorption measurements on SBS block copolymer systems[11] show a quantitatively and qualitatively different behaviour. Therefore we conclude from the ultrasonic absorption, as in the case of dynamic shear viscosities, that there are
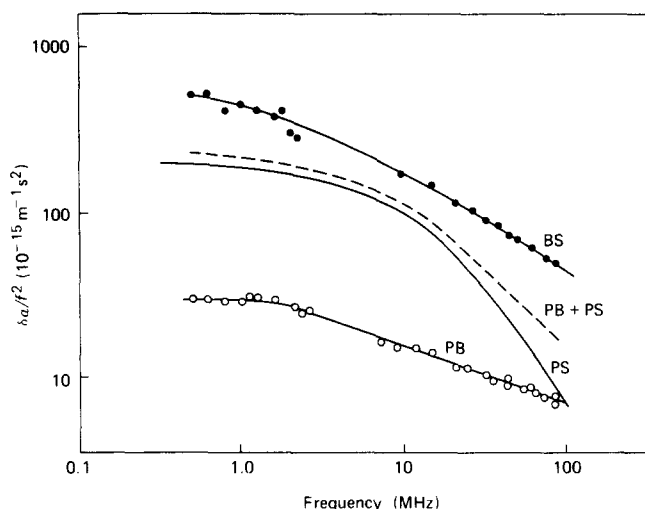
different solution structures for the different types of block copolymers.

In order to answer this question, further studies not only by acoustic methods seem to be necessary.

CONCLUSIONS

For the polybutadiene as well as for the polybutadiene-*block*-polystyrene copolymer solutions the relaxational behaviour could not simply be explained by Rouse–Zimm type motion and local modes of segmental conformational changes. The complexity of the motion requires further dissipation processes to be taken into account, such as perturbations of polymer–polymer or polymer–solvent structures by the sound wave. The measurement of shear and effective viscosity in the systems was useful for gaining a better understanding of the processes involved. Further investigations with a more extensive use of results from other experimental methods would be useful.

ACKNOWLEDGEMENT

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