

Michael Baumgärtel
 Norbert Willenbacher

The relaxation of concentrated polymer solutions

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Dedicated to Prof. Dr. J. Meissner on the occasion of his retirement from the chair of Polymer Physics at the Eidgenössische Technische Hochschule (ETH) Zürich, Switzerland

Dr. M. Baumgärtel (✉)
 Dr. N. Willenbacher
 BASF AG
 Kunststofflabor
 67056 Ludwigshafen, FRG

Abstract The focus of this paper is on the viscoelastic properties of concentrated polymer solutions and polymer melts. Dynamic mechanical measurements were performed on various polystyrene/ethylbenzene solutions with polymer concentrations ranging from 40% up to 100% and temperatures from $T_g + 30^\circ\text{C}$ up to 70°C (230°C for polymer melts). The basis polymers are two commercial grade polystyrenes (BASF) with $M_w = 247$ kg/mol and 374 kg/mol, respectively. To avoid solvent loss due to evaporating during the measurements, a special sealing technique was used.

A phenomenological model which describes quantitatively the relaxation spectrum of concentrated polymer solutions from the flow regime up to the glass transition regime is developed. The relaxation data of the respective polymer melt

and the glass transition temperature of the solution are the only input parameters needed. The temperature dependence is described by a universal, concentration invariant WLF-equation. The relaxation spectra are divided into two parts accounting for the entanglement and the segmental relaxation modes, respectively. The relaxation strength related to the flow and entanglement regime scale with $c^{2,3}$, whereas the segmental relaxation strength does not alter with concentration. All relaxation times change with concentration proportional to $c^{3,5}$. Flow curves can be calculated from these relaxation spectra and thus, our results are useful for engineering applications.

Key words Polymer solution – relaxation – viscosity – scaling – polystyrene

Nomenclature

Roman Symbols

a_T	Time temperature superposition shift factor	–	b_c	Modulus concentration shift factor in the flow regime	–
a_c	Time concentration superposition shift factor in the flow regime	–	b'_c	Modulus concentration shift factor in the glassy regime	–
a'_c	Time concentration superposition shift factor in the glassy regime	–	B	Virial coefficients	–
b_T	Modulus temperature superposition shift factor	–	c	Polymer mass fraction	kg/kg
			c_1	WLF-parameter	–
			c_2	WLF-parameter	K
			g	Relaxation strength of a relaxation mode	Pa
			$G(t)$	Relaxation modulus	Pa
			G'	Storage modulus	Pa

G''	Loss modulus	Pa
G_N^0	Plateau modulus of linear flexible polymers	Pa
$\delta(x)$	Delta function: $\delta(0) = 1$, $\delta(x < > 0) = 0$	—
$h(\gamma)$	Damping function	—
$H(\lambda)$	Relaxation spectrum	Pa
J_N^0	Recoverable compliance	Pa^{-1}
m	Mass	kg
M_c	Critical molecular weight	kg/mol
M_e	Entanglement molecular weight	kg/mol
M_w	Weight average molecular weight	kg/mol
M	Number of datapoints	—
n	Scaling exponent	—
N	Number of discrete relaxation modes	—
T	Temperature	$^{\circ}\text{C}$
T_g	Glass transition temperature	$^{\circ}\text{C}$
V	Volume	l

Greek Symbols

α	Scaling exponent	—
α_f	Thermal expansion coefficient	K^{-1}
β	Scaling exponent	—
γ	Shear deformation	—
$\dot{\gamma}$	Shear rate	s^{-1}
λ	Relaxation time	s
λ_c	Characteristic relaxation time of the Cross model	s
λ_e	Entanglement relaxation time	s
η	Viscosity	Pa s
η_0	Zero shear viscosity	Pa s
Ψ_0	First normal stress coefficient	Pa s^2
ξ	Segmental friction coefficient	—
ω	Frequency	rad/s

Indices

f	Flow and entanglement regime
g	Glass transition regime
i	Count parameter
p	Polymer
ref	Reference state
s	Solvent

Introduction and background

In engineering applications, flow curves (viscosity vs. shear rate) are needed to calculate the pressure drop in pipes, or in polymer reaction processes, the yield in a stirred tank reactor may be correlated from viscosity data. The goal of our work was to develop a phenomenological model which allows the prediction of rheological correlation functions for concentrated polymer solutions from polymer melt data. Such a model should be as simple as possible (easy to use), but at the same time it should reflect polymer physics.

Above the critical molecular weight M_c , the flow behavior of concentrated polymer solutions is dominated by intermolecular polymer chain interactions. As shown in Fig. 1, polymer solutions can be classified into dilute and concentrated systems (Graessley, 1974). Further, one distinguishes between two chain interaction types, entangled and not entangled.

The focus of this paper is on the rheology of concentrated polymer solutions, where the polymer chains are highly entangled. We further restrict ourselves to polymers with linear flexible chains. This implies that the following condition must be fulfilled.

$$M_w \cdot c > M_c \quad (1)$$

We are interested in the relaxation phenomena of such polymer solutions ranging from the flow (terminal) regime up to the glass transition regime. Therefore the relaxation behavior of concentrated polystyrene/ethylbenzene solutions has been studied using dynamic mechanical spectroscopy. Measurements at various polymer concentrations ($c = 40-100\%$), temperatures and two different molecular weights ($M_w = 247 \text{ kg/mol}$ and 374 kg/mol) were performed.

The viscoelastic properties of concentrated polymer solutions as well as polymer melts have been studied extensively during recent decades. A large amount of experimental data and several theoretical concepts are reviewed in Ferry's textbook (Ferry, 1980) and other review papers (Berry et al., 1968; Pearson, 1987).

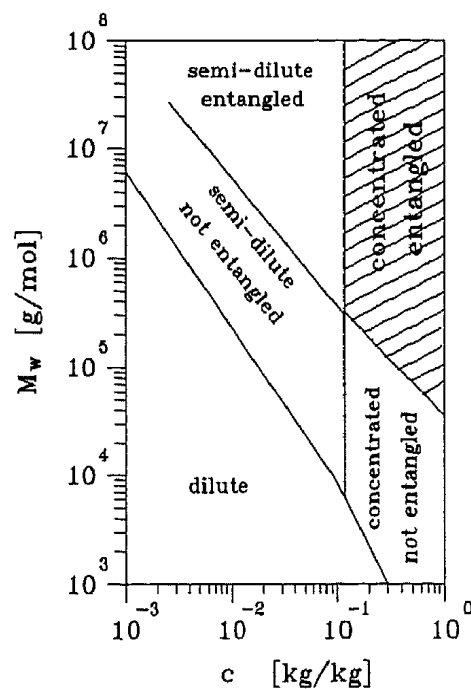


Fig. 1 Scheme of polymer solutions (Graessley, 1974); In the present work we study the rheological behavior of concentrated polymer solutions where the polymer chains are highly entangled

Many experimental as well as theoretical studies support the following expression for the zero shear rate viscosity η_0 of concentrated solutions of linear, flexible polymers

$$\eta_0 = K c^\beta M_w^a \xi(c, T) \quad (2)$$

The molecular weight dependence of η_0 has been investigated for a large number of polymer/solvent systems and turned out to be similar to that for polymer melts.

$$a = 1.0 \quad \text{for } c \cdot M_w < M_c \quad (3)$$

and

$$a = 3.4 \quad \text{for } c \cdot M_w > M_c \quad (4)$$

The monomeric or segmental friction coefficient ξ characterizes the resistance of the surrounding medium to the translational motion of a polymer molecule and is independent of its molecular weight (Graessly, 1974).

The temperature dependence of ξ is described by the WLF or Vogel-Fulcher equation (Vogel, 1921; Fulcher, 1925; Ferry, 1980). Based on the phenomenological free volume theory several concepts have been proposed to account for the concentration dependence of ξ (Kelley and Bueche, 1961; Braun and Kovacs, 1965; Berry, 1966).

The concentration exponent β has been determined for a large number of polymer/solvent systems. Since β is strongly correlated to ξ , the reported values vary in a wide range depending on the procedure used to determine $\xi(c, T)$. For example, for the system polystyrene/ethylbenzene the values of β range from 3.4 (Richards, 1986) to 6.3 (Mendelson, 1980).

The concentration dependence of the plateau modulus G_N^0 can be expressed in terms of a power law

$$G_N^0 \propto c^{\beta_1} \quad (5)$$

with $\beta_1 = 2.1-2.3$ for a large number of concentrated polymer/solvent systems (Graessly, 1981).

Osaki et al. have determined $\beta = 2$ for the system polystyrene/diethylphtalate. Additionally, they have found that the relaxation strength corresponding to the longest relaxation times increase proportional to the third power of c for $c \cdot M_w > 40M_c$ (Osaki, 1975). A rapid increase of the plateau zone with increasing concentration and molecular weight has been reported for the system polystyrene/chlorinated diphenyl (Holmes, 1971).

Nonlinear viscoelastic properties of concentrated polystyrene solutions have been discussed by several authors (see e.g. Forsman, 1986; Osaki, 1993). A broad shear rate range has been investigated in steady shear experiments (Mendelson, 1980) and concentration invariant master curves have been constructed for viscosity vs.

shear rate data (Graessly, 1967). The damping function $h(\gamma)$ characterizing the strain dependence of the relaxation modulus $G(t, \gamma)$ is independent of polymer molecular weight and concentration (Fukuda, 1975).

The model of Doi and Edwards (1978) which is based on de Gennes (1971) reptation theory yields a good description of the slow dynamics of concentrated polymer solutions and melts. The dependence of zero shear rate viscosity on molecular weight ($\eta_0 \propto M_w^3$) is predicted quite well and the predictions for the concentration dependence of the plateau modulus ($G_N^0 \propto c^{2.25}$) as well as for the damping function $h(\gamma)$ are in excellent agreement with experimental data. Nevertheless, the model fails on a short time scale and the calculated decrease of G'' and the leveling off of G' in the plateau and transition zone contradicts experimental observations. Furthermore, the effect of shear thinning in steady shear experiments is overestimated.

Recently, a modification of the Doi-Edwards model has been presented (Kröger and Hess, 1993). Stimulated by nonequilibrium molecular dynamics calculations the alignment of chain ends under shear flow is taken into account, and by adjusting additional alignment parameters the experimental relaxation spectra for concentrated polystyrene solutions (Holmes, 1971) are reproduced very well throughout the whole frequency range.

For engineering applications several empirical correlation functions have been proposed to determine the dependence of viscosity on polymer concentration, temperature and molecular weight (e.g. Harkness, 1982; Kim and Naumann, 1992). For each polymer/solvent system a large amount of data is needed to establish such a model. For the system polystyrene/ethylbenzene Harkness developed the following correlation function

$$\ln \eta_0 = -13.04 + \frac{2013}{T} + M_w^{0.18} \cdot \left[3.915 c - 5.437 c^2 + \left(0.623 + \frac{1387}{T} \right) c^3 \right] \quad (6)$$

Obviously, this model violates the well established scaling law $\eta_0 \propto M_w^{3.4}$ and the temperature dependence does not match the WLF-equation. Therefore, such correlation functions are only valid in a limited parameter range.

Empirical virial equations are also often used to fit isothermal experimental data (Kulicke, 1984):

$$\eta_{sp} = \frac{\eta_0 - \eta_s}{\eta_s} = \sum_k B_k c^{a_k} M_w^{b_k} \quad (7)$$

Note that the parameters of Eq. (7) are temperature dependent.

The phenomenological approach presented here allows to calculate linear viscoelastic material functions as well as flow curves for concentrated polymer solutions from the relaxation data and the WLF-parameters of the respective melt. The only additional information needed is the glass transition temperature of the solution.

Experimental part

In this paper we investigate two commercial BASF polystyrene grades dissolved in ethylbenzene. The ethylbenzene used was of commercial grade without special purification. Solutions containing 40% to 80% polystyrene and the corresponding polystyrene melts were investigated by dynamic mechanical spectroscopy. Glass transition temperatures were obtained independently by differential scanning calorimetry (DSC) and the polymer concentration of the samples was determined by thermogravimetric analysis (TGA). A listing of the samples is given in Table 1.

Dynamic mechanical data for the melts were measured using a RMS 800 (Rheometrics Inc.).

A modified Bohlin CS Rheometer equipped with cone/plate and plate/plate geometry was used for the solutions. To avoid solvent loss during the experiment the polymer solutions were covered with water at temperatures between 0° and 70°C. In the temperature range below 0°C the samples were covered with a low viscosity oil in order to prevent deposition of ice crystals and freez-

Table 1 Polystyrene/ethylbenzene solutions studied in this paper

Polymer	M_w kg/mol	c (TGA) weight %	$M_w c$ kg/mol
PS 374	374	100.0	374
PS 374	374	81.6	305
PS 374	374	71.4	267
PS 374	374	62.6	234
PS 374	374	52.1	195
PS 374	374	42.2	158
PS 247	247	100.0	247
PS 247	247	78.5	194
PS 247	247	71.1	176
PS 247	247	67.2	166
PS 247	247	53.7	133
PS 247	247	40.6	100

Table 2 Time-temperature superposition shift factors of the polystyrene/ethylbenzene solutions. The reference temperatures are marked bold

PS 374				PS 347			
c %	T_m °C	$\log a_T$	$\log b_T$	c %	T_m °C	$\log a_T$	$\log b_T$
100	140	1.42	0.02	100	140	1.43	0.02
	150	0.68	0.00		150	0.64	0.01
	160	0.00	0.00		160	0.00	0.00
	170	-0.54	-0.01		170	-0.54	0.00
	180	-1.01	-0.01		180	-1.00	0.00
	210	-2.06	-0.02		210	-2.03	-0.05
	230	-2.52	-0.03				
	81.6	40	2.94		0.28	78.5	20
60		0.75	-0.05	40	-1.97		-0.23
70		0.00	0.00	70	-3.83		-0.22
80		-0.52	-0.08				
90		-1.05	-0.02				
71.4	-18	4.51	0.24	71.1	5	1.48	0.04
	0	2.08	0.06		25	0.00	0.00
	25	0.00	0.00		40	-0.79	-0.02
	40	-0.72	-0.11		70	-2.02	-0.05
	70	-1.81	-0.15				
62.6	-30	3.50	0.21	67.2	-10	2.38	-0.13
	-13	1.77	0.04		25	0.00	0.00
	0	0.79	0.03		40	-0.58	-0.02
	25	0.00	0.00		70	-1.41	-0.12
	40	-0.55	0.02				
	70	-1.00	-0.08				
52.1	-56	4.84	0.13	53.7	-50	4.14	0.03
	-40	2.68	-0.03		0	0.75	0.13
	-16	1.36	0.05		25	0.00	0.00
	0	0.75	0.02		40	-0.33	-0.07
	25	0.00	0.00		70	-0.85	-0.13
	40	-0.32	-0.06				
42.2	70	-0.83	-0.06	40.6	-50	1.87	0.09
	-58	2.82	0.08		0	0.40	0.00
	-14	0.78	0.06		25	0.00	0.00
	0	0.50	0.07		40	-0.22	-0.05
	25	0.00	0.00				

controlled stress rheometer

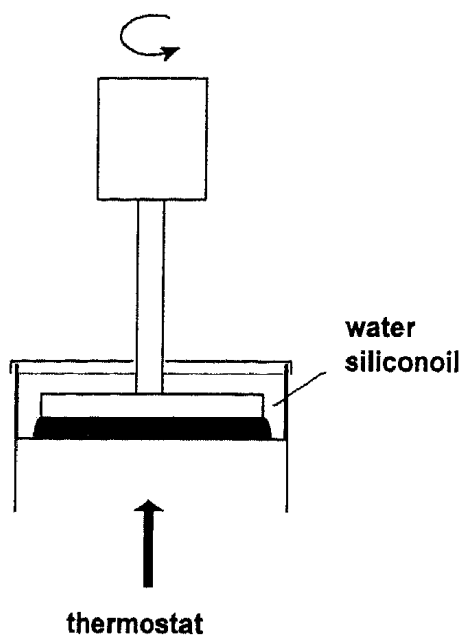


Fig. 2 Experimental setup for the dynamic mechanical spectroscopy on the polymer solutions

Table 3 Discrete relaxation spectrum of the PS 374 melt at a reference temperature of 160 °C, calculated with the IRIS program. The spectrum is split into the contribution of the flow regime and into the contribution of glass transition regime

Flow regime		
i	$g_{i,f}$ Pa	$\lambda_{i,f}$ s
1	$1.476 \cdot 10^4$	$1.403 \cdot 10^{-4}$
2	$1.816 \cdot 10^4$	$1.166 \cdot 10^{-3}$
3	$2.706 \cdot 10^4$	$9.265 \cdot 10^{-3}$
4	$2.885 \cdot 10^4$	$4.325 \cdot 10^{-2}$
5	$4.150 \cdot 10^4$	$2.270 \cdot 10^{-1}$
6	$4.901 \cdot 10^4$	$1.332 \cdot 10^0$
7	$3.983 \cdot 10^4$	$8.093 \cdot 10^0$
8	$2.002 \cdot 10^4$	$4.993 \cdot 10^1$
9	$4.168 \cdot 10^3$	$3.292 \cdot 10^2$
10	$2.529 \cdot 10^2$	$2.590 \cdot 10^3$
Glass transition regime		
i	$g_{i,g}$ Pa	$\lambda_{i,g}$ s
1	$1.160 \cdot 10^7$	$1.403 \cdot 10^{-6}$
2	$7.002 \cdot 10^5$	$1.166 \cdot 10^{-4}$
3	$2.226 \cdot 10^5$	$9.265 \cdot 10^{-4}$
4	$7.737 \cdot 10^4$	$4.325 \cdot 10^{-3}$
5	$2.701 \cdot 10^4$	$2.270 \cdot 10^{-2}$
6	$9.430 \cdot 10^3$	$1.332 \cdot 10^{-2}$
7	$3.294 \cdot 10^3$	$8.093 \cdot 10^{-1}$

ing at the sample surface due to the humidity of the surrounding air. The whole sample geometry was covered with a lid as shown in Fig. 2 to reduce air circulation. Time sweeps were performed to assure that the sample does not change during the experiment.

The Bohlin instrument is temperature controlled by heating/cooling the lower plate. Therefore, a temperature gradient occurs between the upper and lower part of the geometry. This gradient was reduced to 1 K even at temperatures of +70° and -60 °C due to the thermostated cover fluid and the reduced air circulation. The temperature was measured by a thermocouple inside the sample and was kept constant to ± 1 K.

Frequency sweeps at various temperatures were performed. Time-temperature superposition using the IRIS program (Baumgärtel et al., 1989) allows the construction of master curves ranging from the flow regime up to the glass transition regime for all samples (see Table 3). The dynamic data master curves for the two polystyrene melts PS 374 and PS 247 are shown in Fig. 3 at a reference temperature of 160 °C. The reference temperature is selected arbitrarily to be 60 K above the glass transition temperature of polystyrene.

DSC-Measurements were carried out on a DuPont 912 instrument. Samples (about 13 mg in weight) were rapidly cooled down from room temperature to -150 °C and subsequently heated at a rate of 20 °C/min. The glass transition temperature was determined as the temperature where half of the heat flow increment has occurred (mid-point temperature).

Theory and data analysis

Conventionally the polymer concentration in a solution is defined in a volumetric form

$$c' = \frac{m_p}{V} \quad \text{in g/ml} \quad (8)$$

However, this definition is not convenient since this quantity cannot be measured easily. Also, the density of the polymer solution varies slightly with polymer concentration and temperature. Hence the polymer concentration defined by Eq. (8) varies with temperature for a given weight fraction of polymer in solution. We therefore characterize the polymer concentration by the weight fraction of polymer in solution

$$c = \frac{m_p}{m_p + m_s} \quad \text{with: (solvent) } 0 \leq c \leq 1 \quad \text{(polymer)} \quad (9)$$

Polymer melts

As shown by Baumgärtel et al. (1990) the shapes of the G' , G'' curves in the flow regime do not depend on the

Fig. 3 Dynamic moduli master curves of two polystyrene melts with $M_w = 374$ kg/mol and $M_w = 274$ kg/mol. The reference temperature is 160°C

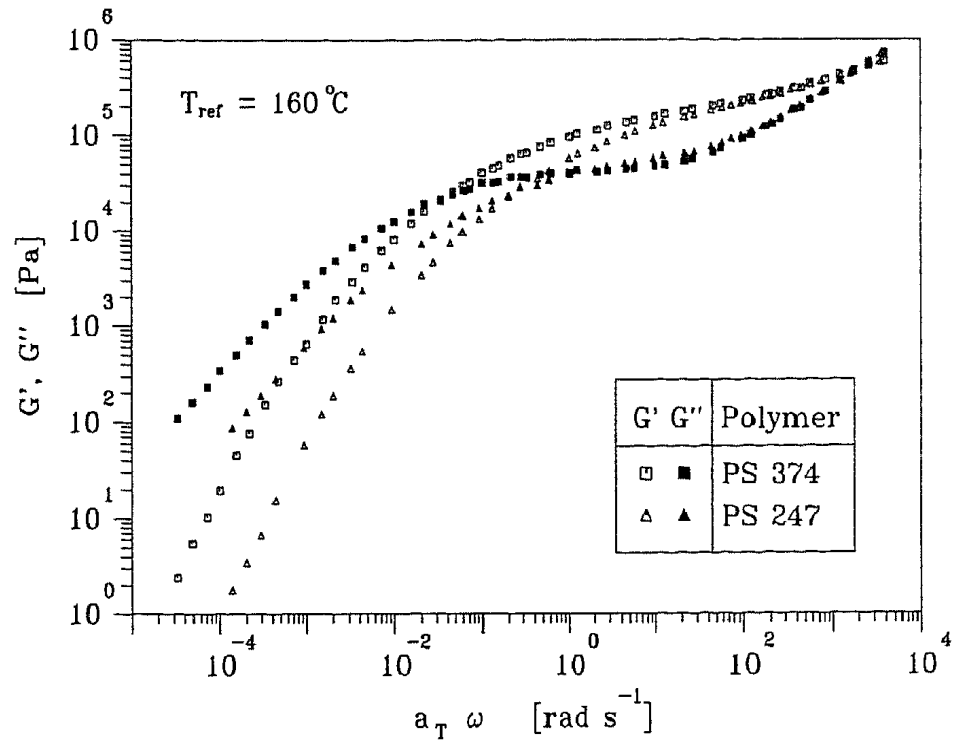
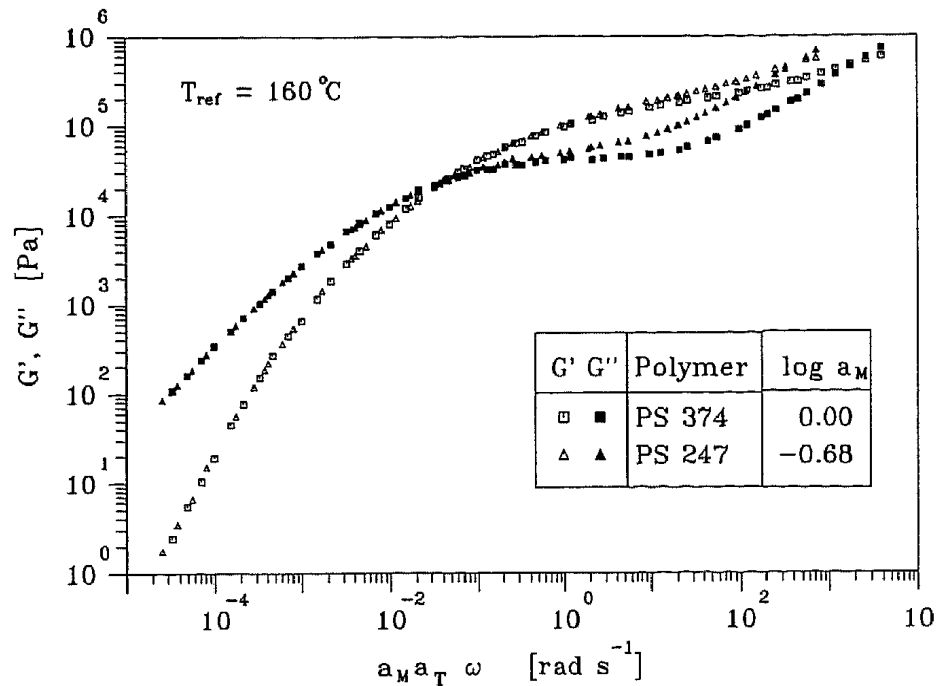


Fig. 4 The dynamic data of PS 247 from Fig. 3 are shifted in the frequency axis (horizontally) in such a way that the data in the flow regime match the data of PS 374



molecular weight if the shape of the molecular weight distribution ($w/\log M$ vs. M) is identical and the molecular weight is greater than the critical molecular weight. However, the shape of the molecular weight distribution significantly affects the shape of the G' , G'' curves in the flow regime. On the other hand, the relaxation modes in the glass transition regime do not depend on the molecular weight distribution and the molecular weight (Ferry, 1980; Baumgärtel, 1992). This is demonstrated in Fig. 4 in

which the master curve of PS 247 (Fig. 3) is shifted horizontally by only a factor a_M such that the flow regimes of PS 374 and PS 247 match. Theoretically, this shift has to follow the well known scaling behavior (Bueche, 1962; Graessley, 1974; Ferry, 1980)

$$a_M = \frac{\eta}{\eta_{ref}} = \left(\frac{M_w}{M_{w,ref}} \right)^{a_M} \quad \text{with } a_M = 3.3 \dots 3.5 \quad (10)$$

To support this model, in Figs. 5a and b the dynamic moduli G' , G'' of the two polystyrene melts PS 247 and PS 374 are split into the contributions of the flow regime (entanglement relaxation) and the glass transition (segmental relaxation).

$$H(\lambda) = H_f(\lambda) + H_g(\lambda) \tag{11}$$

(Baumgärtel et al., 1991) which translates into the power-law behavior of the G' , G'' data in the frequency domain (rhombs in Figs. 5a and b)

$$H_g(\lambda) = n_g G_N^0 \left(\frac{\lambda}{\lambda_e} \right)^{-n_g} \tag{12}$$

The relaxation spectrum at the onset of the glass transition $H_g(\lambda)$ can be correlated by a power-law spectrum

The scaling exponent n_g is determined to be 0.67 (Baumgärtel, 1992).

Fig. 5A The dynamic data master curve of PS 247 (Fig. 5A) can be constructed by a linear superposition of the contribution from the relaxation modes of the flow regime and the contribution from the relaxation modes of the glassy regime

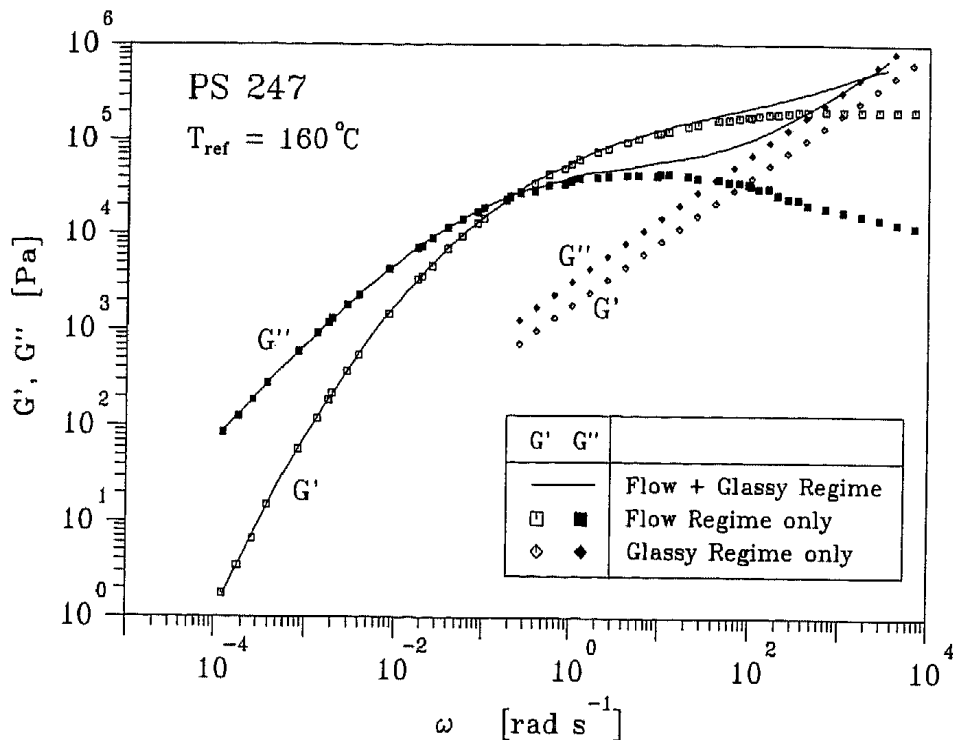
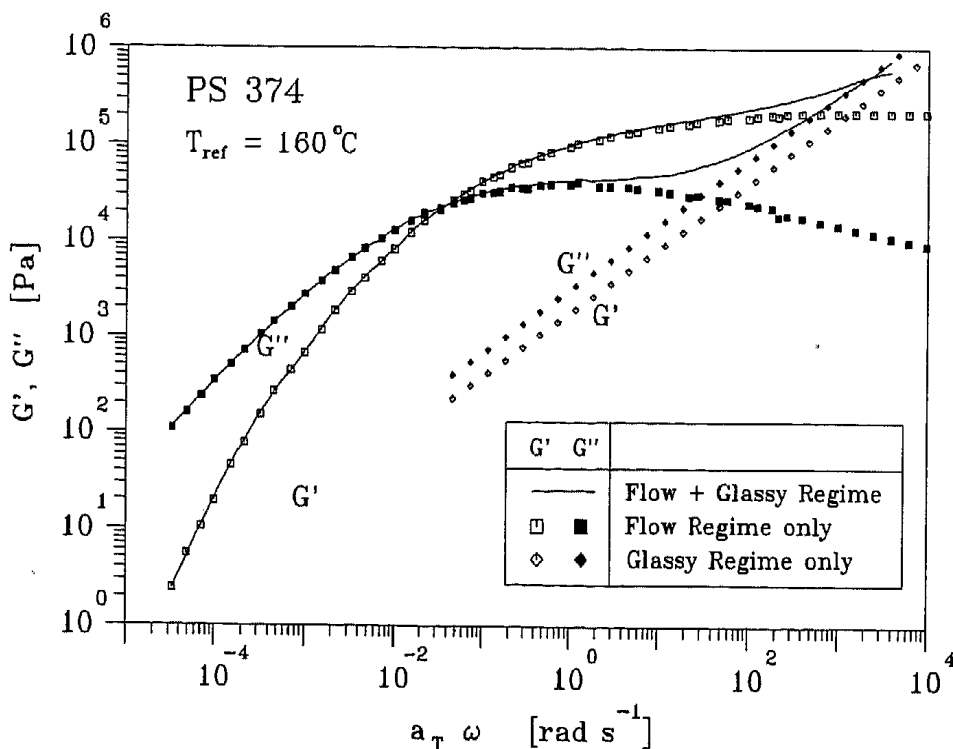


Fig. 5B Analogous to Fig. 5A. The dynamic data master curve of PS 374 (Fig. 5B) can be constructed by a linear superposition of the contribution from the relaxation modes of the flow regime and the contribution from the relaxation modes of the glassy regime. The power law spectrum of the glassy regime is identical to the one in Fig. 5A



The relaxation spectrum in the flow regime $H_f(\lambda)$ depends on the molecular weight distribution. This leads to the G' , G'' curves marked by squares in Figs. 5a and 5b. An analytic equation is only found for monodisperse polymers (Baumgärtel, 1990).

$$H_{f,mono}(\lambda) = \frac{n_e G_N^0 \left(\frac{M_e}{M_w}\right)^{\alpha_M n_e}}{1 - \left(\frac{M_e}{M_w}\right)^{\alpha_M n_e}} \left(\frac{\lambda}{\lambda_e}\right)^{n_e} \cdot \delta\left(1 - \frac{\lambda}{\lambda_e} \left(\frac{M_e}{M_w}\right)^{\alpha_M}\right) \quad (13)$$

The parameters for polystyrene are found to be $n_e = 0.23$, $G_N^0 = 214$ kPa and $\lambda_e = 5.9 \cdot 10^{-4}$ s.

A linear superposition of the G' , G'' curves marked by the squares and the rhombs reproduce the experimental data (marked by the lines in Fig. 5a and b).

In practice, the continuous form of the relaxation spectra is cumbersome to use, since the computation of related material functions like G' , G'' , J' , J'' requires numerical integration of the relaxation spectrum from $\lambda = 0$ to infinity. Therefore, the use of discrete relaxation spectra is preferable:

$$H(\lambda) = \sum_{i=1}^N g_i \lambda_i \delta(\lambda - \lambda_i) \quad (14)$$

The interrelation between discrete and continuous relaxation spectra is described in detail by Baumgärtel et al. (1990). The discrete relaxation spectra of PS 374 is listed in Table 3. It is split according to Eq. (11) into the spectrum for the flow and entanglement regime $g_{i,f}$, $\lambda_{i,f}$ (determined from the data points marked by squares in Fig. 5b) and the spectrum for the glassy regime $g_{i,g}$, $\lambda_{i,g}$ (determined from the data points marked by rhombs in Fig. 5b). The linear superposition of the two spectra describes the G' , G'' data in Fig. 5b.

Polymer solutions

The dynamic moduli master curves of the polymer solutions are shown in Fig. 6a and b. The reference temperatures are chosen arbitrarily. As demonstrated in Fig. 7a and b, the shapes of the G' , G'' data and hence the relaxation spectra in the flow regime are not altered by the solvent (analogue to Fig. 4). Analogous to the polymer melt model, we propose that the relaxation spectrum of polymer solutions can also be modeled by a linear superposition of a power-law spectrum for the glassy regime and a spectrum depending on the molecular weight distri-

bution. The different upturns in the high frequency regime can be explained by different time concentration shift factors for the relaxation modes of the flow regime (a_c , b_c) and for the relaxation modes of the glass transition regime (a'_c , b'_c). The shift of the spectra of polymer solution with respect to the polymer melt can be written in a general form

$$H(\lambda) = b_T b_c H_{f,melt} \left(\frac{\lambda}{a_T a_c}\right) + b_T b'_c H_{g,melt} \left(\frac{\lambda}{a_T a'_c}\right) \quad (15)$$

Temperature dependence a_T

First, the temperature dependence of the relaxation modes has to be analyzed. The temperature dependence of rheological properties like the viscosity or relaxation times for polymer melts or polymer solutions is usually described by the Vogel-Fulcher-equation (Vogel, 1921) or WLF-equation (Williams, Landel, Ferry, 1955):

$$\log_{10} a_T = \frac{-c_1(T - T_{ref})}{c_2 + T - T_{ref}} \quad (16)$$

At the so-called Vogel temperature, $T_\infty = T_{ref} - c_2$, Eq. (16) diverges to infinity.

Equation (16) can be rewritten by defining $T_{ref} = T_g + \Delta T$

$$\log a_T = \frac{-c_1(T - T_g - \Delta T)}{c_2 + T - T_g - \Delta T} \quad (17)$$

T_g varies strongly with concentration, while ΔT is kept constant. Note that the frequently used Arrhenius type of correlation for $\log a_T$ is only valid at temperatures far above the glass transition temperature.

Our analysis of the shift factors a_T is based on the assumption that the parameters c_1 and c_2 of the Vogel or WLF-equation (Eq. (16)), are independent of the solvent content in concentrated polymer solutions or equivalently, the thermal expansion coefficient α_f of the free volume is independent of the solvent content. In the review paper of Berry and Fox (1968) the WLF-parameters for various polymer solvent systems are discussed showing a slight dependence of α_f on polymer concentration, which can be neglected in most practical cases. The temperature dependence of the relaxation behavior is therefore primarily determined by the depression of the glass transition temperature T_g due to the solvent. For the system polystyrene/ethylbenzene these assumptions are confirmed by the results of Richards and Prud'homme (1986). They have found that α_f increases only slightly with increasing solvent content (in the concentration range $c > 50\%$) and that T_∞ decreases drastically on dilution. However, in contrast to our analysis they took into account the slight change in the

Fig. 6A Dynamic data mastercurves of PS 247 solutions with varying content of polymer *c*. The reference temperatures are chosen arbitrarily

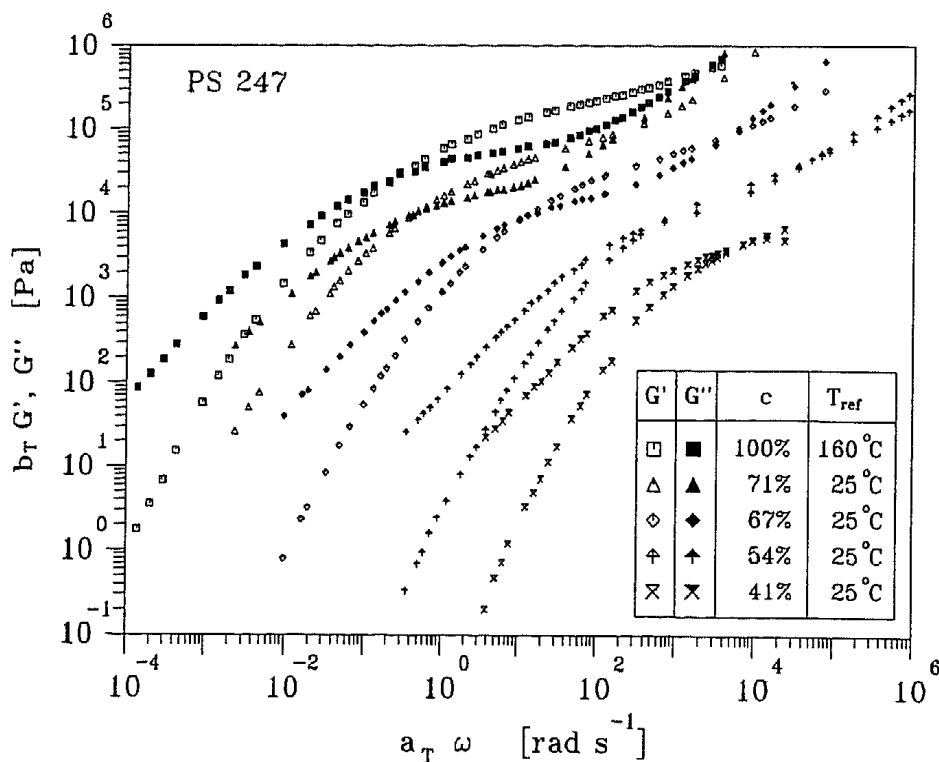
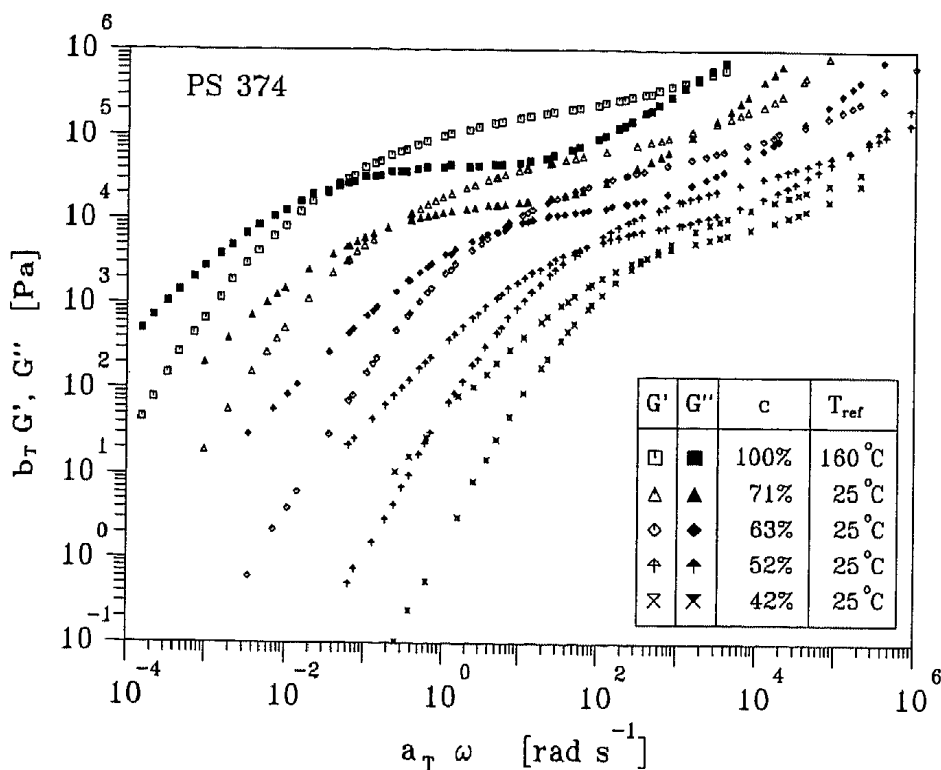


Fig. 6B Dynamic data mastercurves of PS 374 solutions with varying content of polymer *c*. The reference temperatures are chosen arbitrarily



free volume in their evaluation of the concentration and temperature dependence of the zero shear rate viscosity.

In the first step of our analysis, the WLF-parameters c_1 and c_2 for a reference temperature of 160 °C are determined from the polystyrene melt data of the samples PS 247 and PS 374.

$$c_1 = 6.37$$

(18)

$$c_2 = 107.0 \text{ K} \quad (19)$$

The glass transition temperature of the pure polystyrene melt $T_{g,p}$ is assumed to be 100 °C (Ferry, 1980).

The second step is the determination of the concentration dependence of the glass transition temperature. Corresponding data for several polystyrene/solvent systems are collected in Ferry's textbook (1980). For these systems

Fig. 7A Dynamic data mastercurves of PS 247 solutions from Fig. 6A are shifted (horizontally and vertically) in such a way that they form a "concentration"-master curve in the flow regime

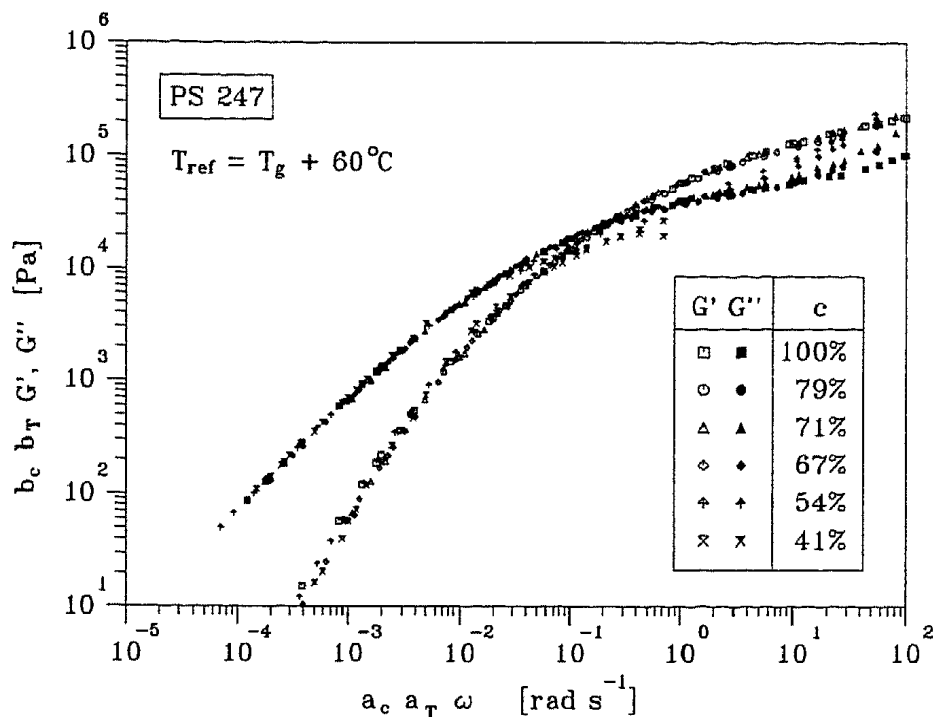
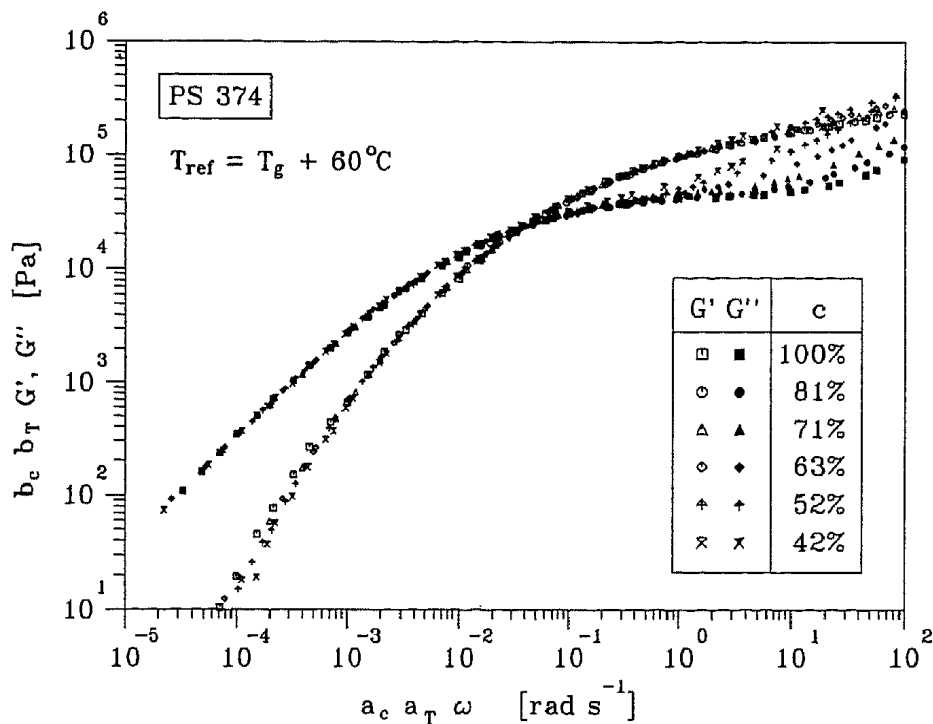


Fig. 7B Dynamic data mastercurves of PS 374 solutions from Fig. 6B are shifted (horizontally and vertically) in such a way that they form a "concentration"-master curve in the flow regime



the decrease of T_g on dilution is linear only in a small concentration range ($c = 80\% - 100\%$). Therefore the following quadratic form is proposed for the concentration dependence of T_g (Ferry, 1980; Braun et al., 1965).

$$T_g = (1-c)T_{g,s} + cT_{g,p} + k_v c(1-c) \quad (20)$$

this limit T_g should be independent of the polymer concentration:

$$\lim_{c \rightarrow 0} \frac{\partial T_g}{\partial c} = 0 \quad (21)$$

From a physical point of view an additional constraint could be added for infinitely dilute polymer solutions. In

This boundary condition is satisfied by the following correlation

$$T_g = T_{g,s} + (T_{g,p} - T_{g,s})c^n \quad (22)$$

which reduces to Eq. (20) for $k_v = T_{g,p} - T_{g,s}$ and $n = 2$.

From the experimental time temperature shift factors of the polymer solution data, the glass transition temperature of the solvent $T_{g,s}$ and the parameter n of Eq. (22) can be determined using non-linear least square minimization of the following equation:

$$\sum_{j=1}^M \left(\log a_{T,j} - \left(\frac{-c_1(T_j - T_g - \Delta T)}{c_2 + T_j - T_g - \Delta T} - \frac{-c_1(T_{ref,m} - T_g - \Delta T)}{c_2 + T_{ref,m} - T_g - \Delta T} \right) \right)^2 = \min. \quad (23)$$

The measured shift factors $a_{T,j}$ in Eq. (23) correspond to a time temperature shift from T_j with respect to an arbitrarily chosen reference temperature $T_{ref,m}$ for the according polymer solution (see Table 2). The constants c_1 , c_2 were determined previously from polymer melt data (Eqs. (18), (19)). ΔT was arbitrarily chosen to be 60 K. Inserting T_g from Eq. (22) the data regression was performed using all experimental data of PS 247 and PS 374 simultaneously (Table 2). The following values for the parameters $T_{g,s}$ and n were obtained.

$$T_{g,s} = -169^\circ\text{C} \quad (24)$$

$$n = 2.0 \quad (25)$$

This value of $T_{g,s}$ is in excellent agreement with the value of $T_{g,s} = -162^\circ\text{C}$ determined from a previous analysis of viscosity data (Faerber et al. 1970). The value of -154°C estimated from the general rule for asymmetric molecules, $T_g = \frac{2}{3}T_m$ with $T_m = -95^\circ\text{C}$ for ethylbenzene, is also very close. Since $n = 2.0$ the correlation functions (20) and (22) are equivalent.

Table 4 Glass transition temperatures determined from DSC and rheology

Polymer	c (TGA) weight %	T_g (DSC) $^\circ\text{C}$	T_g (Rheo) $^\circ\text{C}$
PS 374	100.0	100	100
PS 374	81.6	20	11
PS 374	71.4	-18	-31
PS 374	62.6	-46	-62
PS 374	52.1	-75	-95
PS 374	42.2	-97	-120
PS 247	100.0	100	100
PS 247	78.5	8	-2
PS 247	71.1	-19	-32
PS 247	67.2	-32	-46
PS 247	53.7	-71	-90
PS 247	40.6	-100	-123

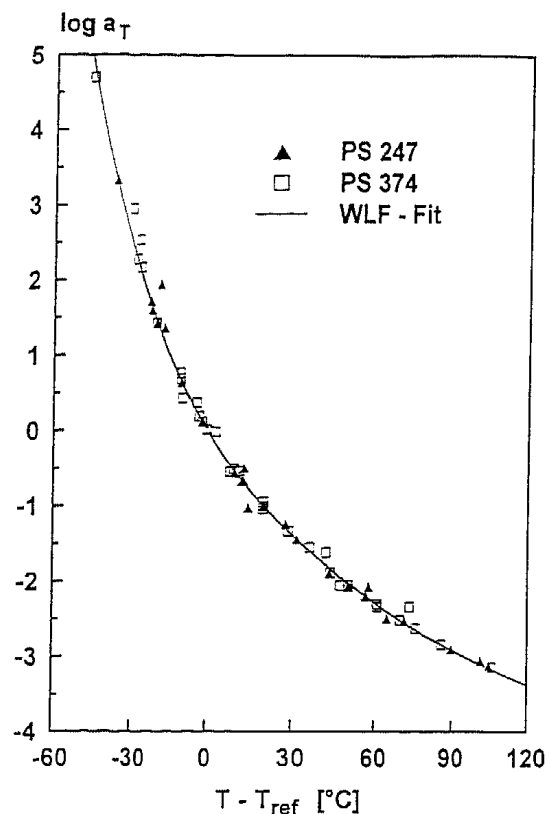


Fig. 8 The time temperature superposition shift data a_T of the polystyrene/ethylbenzene solutions (data of Table 2) can be reduced to a master curve which can be correlated by a single WLF-fit. The WLF parameter c_1 and c_2 are determined from the polystyrene melt data

The glass transition temperatures determined by rheology (Eq. (22)) and the results obtained from DSC measurements are in quite good agreement (see Table 4). Nevertheless, the rheological data are systematically lower than those from thermal analysis. In part, this is due to the fact, that the DSC data were not corrected with respect to cooling and heating rate effects (enthalpy relaxation) and finite thermal conductivity of the sample (Rieger, 1995). The deviations increase with decreasing absolute value of T_g (decreasing polymer content). A more detailed discussion of the differences between the T_g values obtained by DSC and rheology is not tried here, and our further analysis of the relaxation spectra of polymer solutions is purely based on the rheologically determined T_g data.

Figure 8 shows all time temperature shift factors now reduced to a reference temperature $T_{ref} = T_g + \Delta T$, with T_g calculated from Eq. (22) using the results of the minimization of Eq. (23). Obviously, all these data fit quite well to a single WLF-equation with parameters c_1 and c_2 taken from polymer melt data. Note that experimental errors in the concentration were neglected.

Time concentration shift

In Figs. 9a to 9d the dynamic data of the polymer solutions are replotted such that the reference temperature is $\Delta T = 600$ K above the corresponding glass temperature. One now observes a systematic shift of the G' , G'' curves of the polymer solutions with respect to the polymer melt data. The flow regime is shifted horizontally by a shift

factor a_c and vertically by a shift factor b_c . The glassy modes are shifted horizontally by a shift factor a'_c . The concentration dependence of these time concentration shift factors are shown in Fig. 10a to 10c (symbols). Simple scaling laws are found (lines in Figs. 10a to 10c)

$$a_c = c^{\alpha_1} \quad \text{with} \quad \alpha_1 = 3.5 \pm 0.2 \quad (26)$$

Fig. 9A The dynamic data of the polystyrene solutions of Fig. 6A are replotted at a defined temperature above the glass temperature of the corresponding polymer solution (iso-free-volume state). One observes a concentration dependent shift of the curves

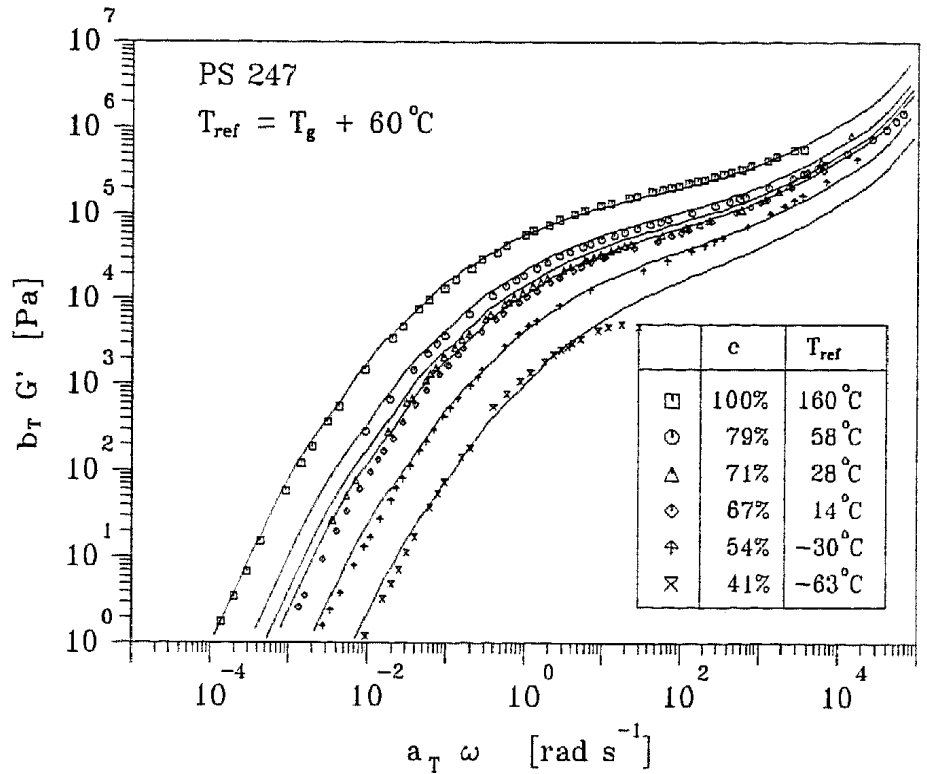


Fig. 9B Loss modulus corresponding to the curves in Fig. 9A

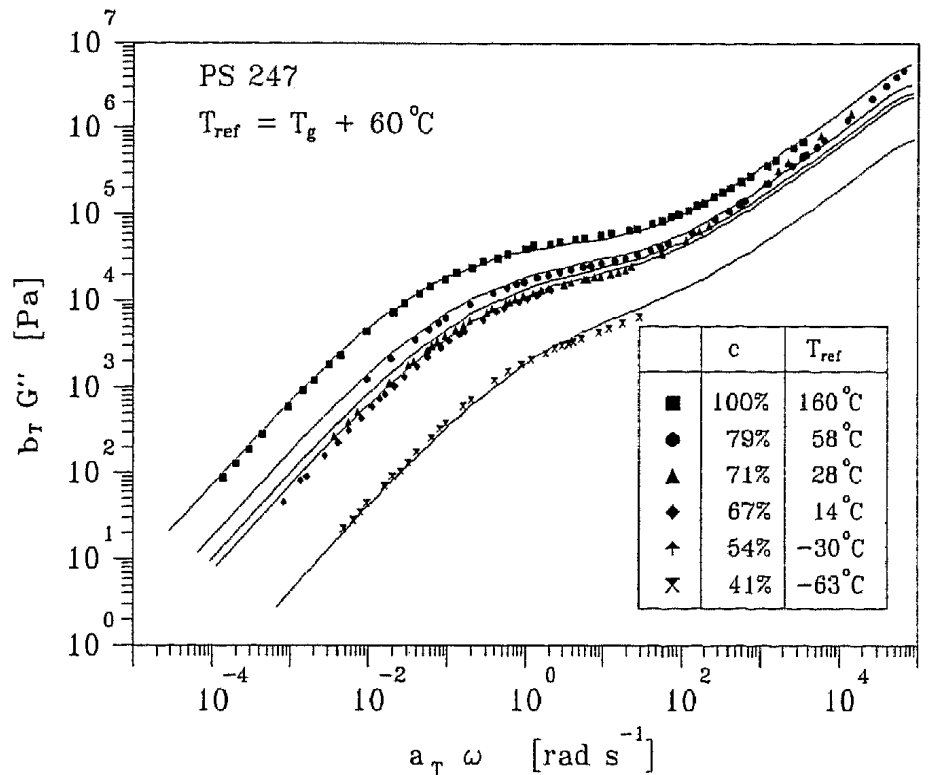


Fig. 9C The dynamic data of the polystyrene solutions of Fig. 6B are replotted at a defined temperature above the glass temperature of the corresponding polymer solution (iso-free-volume state). One observes a concentration dependent shift of the curves

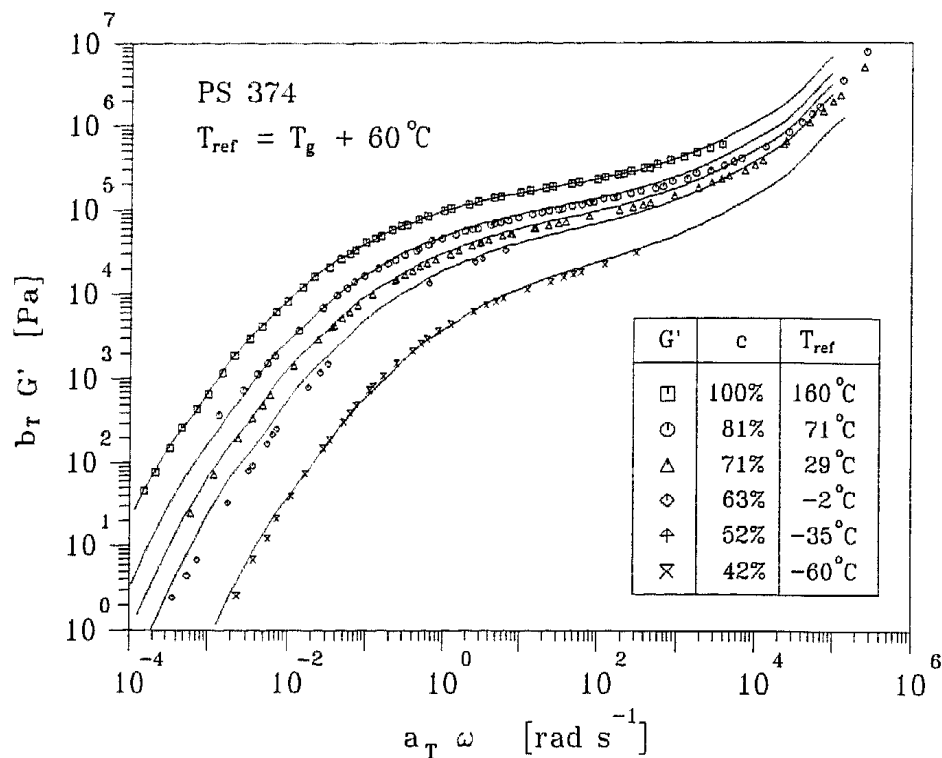
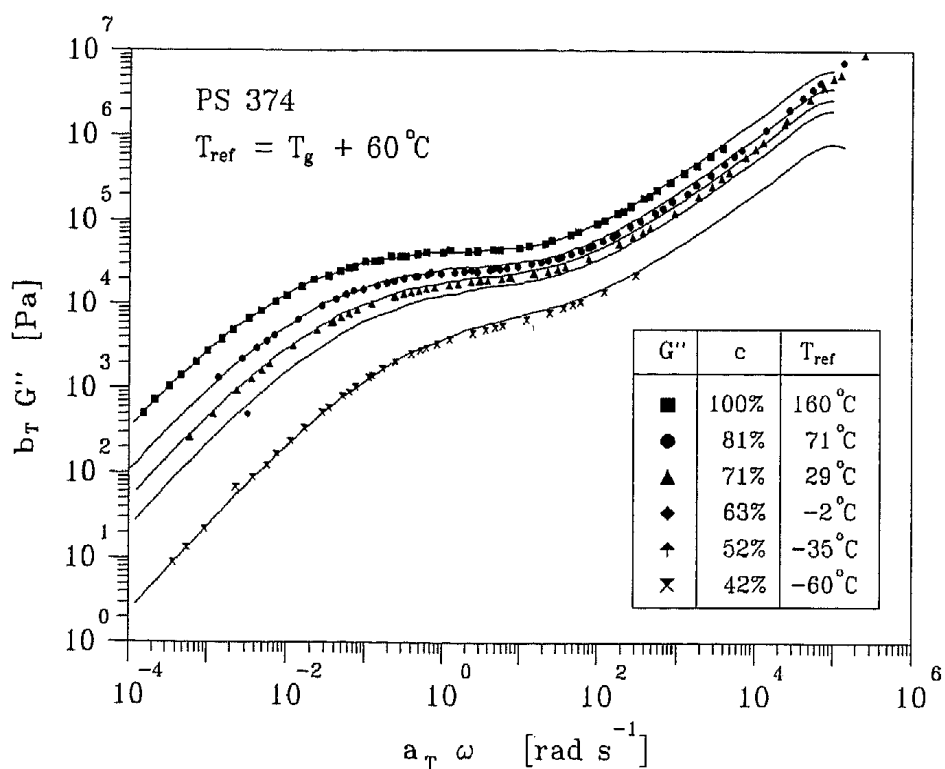


Fig. 9D Loss modulus corresponding to the data in Fig. 9C



$$b_c = c^{\beta_1} \quad \text{with} \quad \beta_1 = 2.2 \pm 0.2 \quad (27)$$

$$a'_c = c^{\alpha_2} \quad \text{with} \quad \alpha_2 = 3.5 \pm 0.2 \quad (28)$$

Equation (27) confirms that the scaling exponent for the plateau modulus given in Eq. (5) holds for the complete relaxation spectrum in the flow and entanglement regime.

Since the relaxation spectrum of the glass transition regime is a power-law, one could also define the horizontal shift $\log a'_c$ to be zero and introduce a vertical shift b'_c

$$b'_c = c^{\beta_2} \quad \text{with} \quad \beta_2 = n_g \alpha_2 = 2.3 \pm 0.2 \quad (29)$$

This question will be discussed in a subsequent paper.

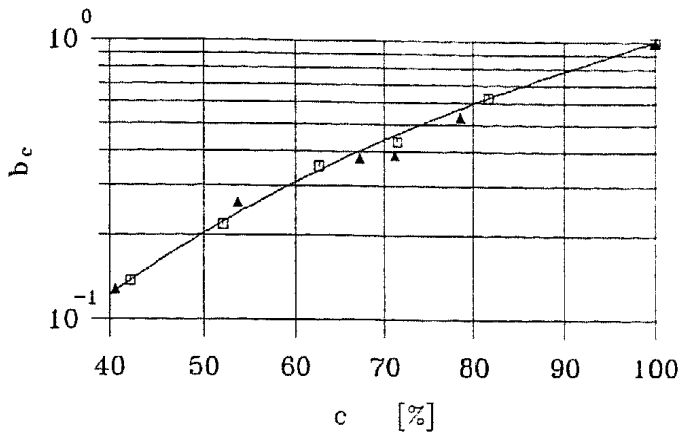


Fig. 10A Concentration dependent shift factor of the relaxation strength $g_{i,f}$ (plateau modulus) at $R_{ref} = T_g(c) + \Delta T$ from Figs. 9A to 9D. The shift factors marked by squares correspond to the PS 374 data and the shift factors marked by triangles correspond to the PS 247 data

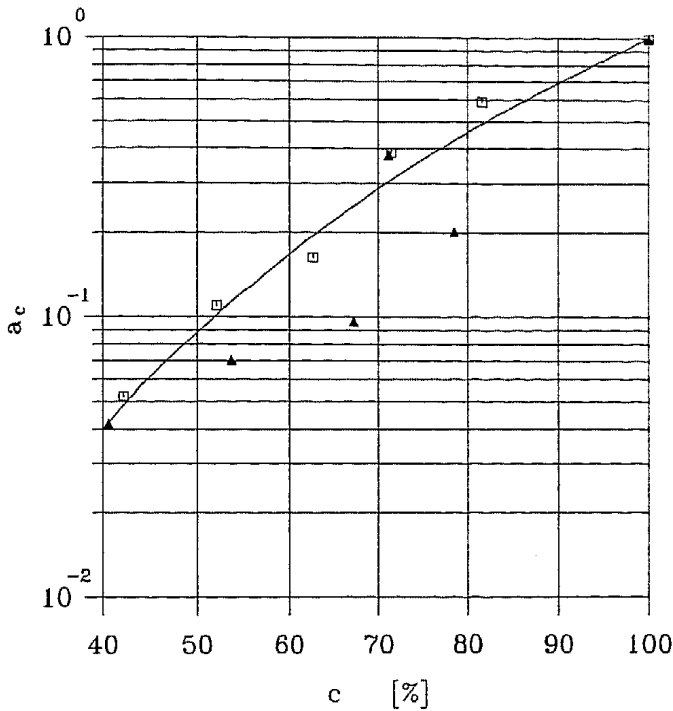


Fig. 10B Concentration dependent shift factor of the relaxation times $\lambda_{i,f}$ at $T_{ref} = T_g(c) + \Delta T$ from Figs. 9A to 9D

So far, we expect that the parameters α_1 , β_1 and α_2 are not dependent on the polymer-solvent system. However, this has to be proven experimentally.

Since the shape of the dynamic data vs. frequency curves in the flow and entanglement regime is independent of solvent concentration, the relaxation times and the relaxation strength of the discrete relaxation modes are shifted in the following manner:

$$\lambda_{i,f}[T, c, M_w] = \frac{\lambda_{i,f,ref}[T_{ref}, c = 1, M_{w,ref}]}{a_T[T, c] a_c[c] a_M[M_w]} \quad (30)$$

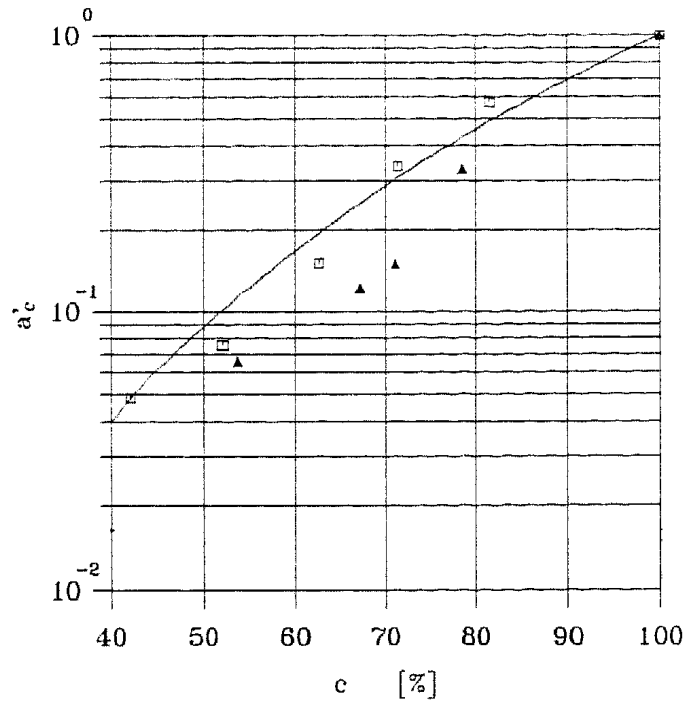


Fig. 10C Concentration dependent shift factor of the relaxation times $\lambda_{i,g}$ in the glass transition regime at $T_{ref} = T_g(c) + \Delta T$ from Figs. 9A to 9D

$$g_{i,f}[T, c] = b_T[T] b_c[c] g_{i,f,ref}[T_{ref}, c = 1] \quad (31)$$

In the glassy regime the following scaling is valid:

$$\lambda_{i,g}[T, c, M_w] = \frac{\lambda_{i,g,ref}[T_{ref}, c = 1, M_{w,ref}]}{a'_c[c] a_T[T, c]} \quad (32)$$

$$g_{i,g}[T, c] = b_T[T] g_{i,g,ref}[T_{ref}, c = 1] \quad (33)$$

Combining the results (Eq. (20)–Eq. (33)), one can predict the viscoelastic behavior of concentrated polymer solutions from the flow regime up to the glass transition from the viscoelastic data of the polymer melt (solid lines in Figs. 9a to 9d).

Application

Rheological constants of polymer solutions can be predicted from the data of the corresponding melts. Especially for engineering purposes, a simple correlation function for the zero shear viscosity which can be derived from our model is extremely useful.

$$G_N^0 = \sum g_i = b_c b_T G_{N,ref}^0 \approx c^{\beta_1} G_{N,ref}^0 \quad (34)$$

$$\eta_0 = \sum g_i \lambda_i = a_s a_c a_T b_c b_T \eta_{0,ref}$$

$$= \eta_{0,ref} \left(\frac{M_w}{M_{w,ref}} \right)^{a_s c^{\alpha_1 + \beta_1}} 10^{-c_1 (T - T_g[c] - \Delta T)^{\gamma_1} (c_2 + T - T_g[c] - \Delta T)}$$
 (35)

$$\psi_{1,0} = \sum g_i \lambda_i^2 = a_T^2 a_c^2 a_s^2 b_c b_T \psi_{1,0,ref}$$
 (36)

$$J_e^0 = \frac{\sum g_i \lambda_i^2}{(\sum g_i \lambda_i)^2} = \frac{1}{b_c b_T} J_{e,ref}^0 \approx c^{-\beta_1} J_{e,ref}^0$$
 (37)

Note that the form of Eq. (35) is identical to the one used by Richards and Prud'homme (1986). In their analysis a slight increase of the thermal expansion coefficient of the free volume has been taken into account, resulting in a concentration dependence of the WLF-parameters c_1 and c_2 . As a consequence, they did obtain a much smaller scaling exponent $\alpha_1 + \beta_1 = 3.8$. A typical plot of zero shear viscosity vs. polymer concentration of polystyrene/ethylbenzene solutions is shown in Fig. 11.

A quantity often considered is the product of the plateau modulus and the recoverable compliance. In agreement with the results of Graessley (1974) and others, our model predicts that in concentrated polymer solutions, this product is independent of the solvent content:

$$G_N^0 J_e^0 (\text{solution}) = G_{N,ref}^0 J_{e,ref}^0 (\text{melt})$$
 (38)

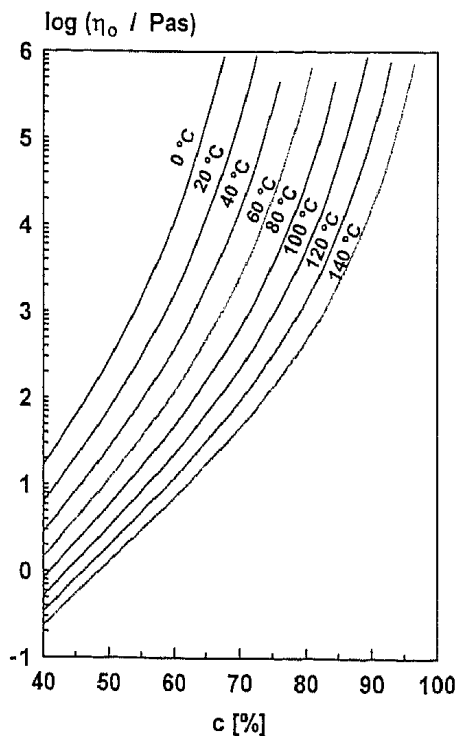


Fig. 11 Dependence of the zero shear viscosity of a polystyrene with $M_w = 247$ kg/mol dissolved in ethylbenzene on solvent content and temperature. The curves are calculated using Eq. (35)

Flow curves of polymer solutions

For engineering purposes the flow curve (shear rate dependence of the viscosity) is needed. Several heuristic relations have been proven to be successful in predicting $\eta(\dot{\gamma})$ from relaxation data.

The Cox-Merz-relation (Cox and Merz, 1958) can convert dynamic mechanical data, G' , G'' , directly into flow-curves or, if the spectrum is available, the parameters g_i , λ_i may be used:

$$\eta[\dot{\gamma}, T, c] = \eta^*[\omega] \Big|_{\omega = \dot{\gamma}} = \frac{1}{\dot{\gamma}} \sqrt{G'^2 + G''^2} \Big|_{\omega = \dot{\gamma}}$$

$$= \frac{1}{\dot{\gamma}} \sqrt{\left(\sum \frac{g_i \lambda_i^2 \dot{\gamma}^2}{1 + \lambda_i^2 \dot{\gamma}^2} \right)^2 + \left(\sum \frac{g_i \lambda_i \dot{\gamma}}{1 + \lambda_i^2 \dot{\gamma}^2} \right)^2}$$
 (39)

A second relation has been suggested by Gleissle (1980)

$$\eta[\dot{\gamma}, T, c] = \sum g_i \lambda_i (1 - e^{-1/(\dot{\gamma} \lambda_i)})$$
 (40)

If no relaxation data are available, flow curves can be calculated using a generalized power law equation introduced by Cross (1968):

$$\eta = \frac{\eta_0}{1 + (\lambda_c \dot{\gamma})^{n_c}}$$
 (41)

The model parameters determined from the flow curve of the pure polymer melt PS 374 are given in Table 5. Note, that this parameter set is only valid for a given polydispersity M_w/M_n . Applying the time concentration shift to the parameters of the Cross-model yields:

$$\eta[\dot{\gamma}, T, c, M_w] = \frac{a_s a_c a_T b_c b_T \eta_{0,ref}}{1 + (\dot{\gamma} a_s a_c a_T \lambda_{c,ref})^{n_c}}$$
 (42)

This equation enables us to calculate the flow curves of the corresponding polymer solutions. A test of our model is shown in Fig. 12. The flow curve of a solution with $c = 67\%$ (PS 374) is measured with a capillary viscometer ($D = 0.62$ mm; $L/D = 242$). The lines are calculated according to Eqs. (39), (40) and (41). The agreement is excellent, if one considers that the viscosity of the solutions is several decades smaller than the viscosity of the corresponding polymer melt.

Table 5 Parameters of the Cross-model for solutions of polystyrene in ethylbenzene

$M_{w,ref}$	374	kg/mol
$\eta_{0,ref}$	$3.31 \cdot 10^6$	Pa s
$\lambda_{c,ref}$	90	s
n_c	0.77	—

Fig. 12 The experimentally determined flow curve (capillary viscometer) of a polystyrene solution with $c = 67\%$ is compared to the model prediction:

⊖: Conversion of the dynamic data of the solution using the Cox-Merz-Relation.

M: Calculated from dynamic data of the melt using the scaling relations derived in this paper. ⊖: The flow curve of the polymer melt (converted from the dynamic data using the Cox-Merz-Relation) is first correlated with the Cross-Model and then shifted using the scaling relations derived in this paper

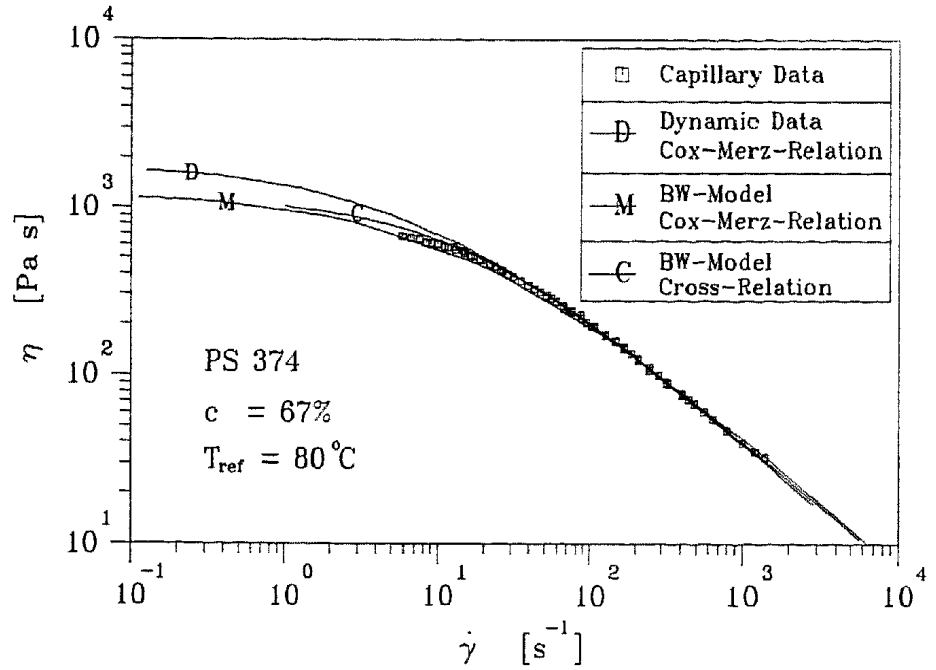
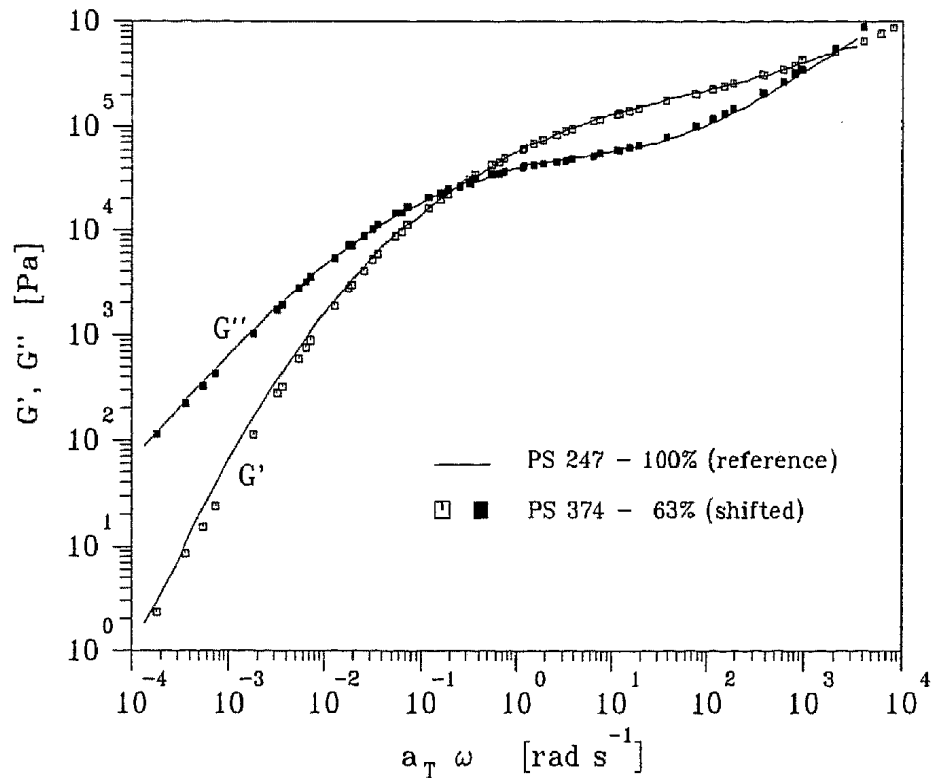


Fig. 13 Curiosity - The shape of the relaxation spectrum of a polystyrene melt with $M_{w,1} = 247\text{ kg/mol}$ and a polystyrene solution with the same average molar mass $M_{w,2}c = M_{w,1}$ are identical



Curiosity

For $\beta_1 = \beta_2$ and $\alpha_M = \alpha_1$ our scaling relations predict that the shape of the G' , G'' vs. ω curves are the same for a polymer melt (molecular weight $M_{w,1}$) and a polymer solution (molecular weight of polymer $M_{w,2}$) with a polymer concentration c if the shape of the molecular weight distribution ($w \text{ dlog } M$ vs. $\log M$) is identical and

the "average" molecular weight of the polymer solution is equal to the molecular weight of the polymer: $M_{w,1} = M_{w,2} c$. Off course, the absolute position of the curves varies as shown by the model described before. This is demonstrated in Fig. 13.

Summary and conclusion

Since no quantitative correct theoretical model predicting the viscoelastic behavior of polymer melts and concentrated polymer solutions has been found yet, we decided to derive a phenomenological model which describes experimental data over a wide frequency range.

The viscoelastic properties of polymer melts and concentrated polymer solutions can be modeled by a linear superposition of two relaxation time spectra, one to describe the flow and entanglement regime, $H_f(\lambda)$, and one to describe the glass transition regime, $H_g(\lambda)$. The shape of the relaxation spectrum $H_f(\lambda)$ depends on the molecular weight distribution but not on the weight average molecular weight M_w (as long as $M_w > M_c$) and not on the solvent content (for concentrated solutions). The relaxation spectrum $H_g(\lambda)$ can be described by a power-law spectrum. $H_g(\lambda)$ does not depend on M_w as long as $M_w > M_c$. The relaxation times and strength of $H_f(\lambda)$ and $H_g(\lambda)$ are shifted uniformly as a function of polymer concentration and temperature. A time-concen-

tration superposition is introduced analogous to the well known time-temperature superposition. Simple scaling laws are found for the time-concentration superposition. The relation strength related to the flow and entanglement regime scale with $c^{2.3 \pm 0.2}$, thus including the well-known relaxation $G_N^0 \propto c^{2.2}$. The scaling exponent found for the relaxation times is 3.5 ± 0.2 . Since the same scaling law holds for the molecular weight dependence of the longest relaxation times, the shape of the relaxation spectrum of a solution of concentration c and molar weight M_w is similar to that of the respective melt with molecular weight $M' = c \cdot M_w$.

The results are especially important for engineering applications. For example, the flow curve of a concentrated polymer solution for any molecular weight, polymer concentration and temperature can be predicted from polymer melt data.

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