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Viscoelastic Properties of Narrow-Distribution Poly(methyl methacrylates)

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ABSTRACT: The viscoelastic properties of two series of poly(methyl methacrylates) (PMMA) with different tacticities and very narrow molecular weight distributions were measured in the molten state at different temperatures by means of oscillatory rheometry. Zero-shear viscosity η_0, steady-state shear compliance $J_e°$, and plateau modulus $G_N°$ were obtained from the resulting master curves for the storage modulus G' and loss modulus G''. Relaxation time spectra $h(\tau)$ were calculated by a nonlinear regularization method and could be used to determine the terminal relaxation time τ_0. The molecular weight and polydispersity dependence of these parameters agrees with existing empirical rules for linear amorphous polymers. Stereoregularity, however, has a great influence on η_0 and τ_0. The entanglement molecular weight M_e and the critical molecular weight M_c seem to vary with the tacticity as well. These results are possible explanations for some contradicting or inconsistent literature data concerning PMMA.

Introduction

The rheological behavior of polymers is a consequence of the molecular chain structure and corresponding dynamical processes. This is not only of academic interest for understanding molecular motions but also of utmost importance in processing, in tailoring, and—a very recent development—in characterizing industrial polymers. During the last two decades, some macroscopically measured viscoelastic material parameters such as zero-shear viscosity η_0, terminal relaxation time τ_0, steady-state shear compliance $J_e°$, and plateau modulus $G_N°$ have been successfully related to the molecular weight and polydispersity of linear homopolymers. For example, the zero-shear viscosity η_0 scales in the following manner with the molar mass M:

$$\eta_0 \propto M^1 \qquad \text{if } M < M_c \tag{1a}$$

$$\eta_0 \propto M^{3.4} \qquad \text{if } M > M_c \tag{1b}$$

where M_c is the critical molar mass for entanglement coupling. In the real case of polydisperse samples, M is assumed to be the weight-average molecular weight M_w. This relation holds for linear polymers except for extremely broad blends.[1,2] Up to now, only PMMA deviates significantly from these empirical findings. Masuda, Kitagawa, and Onogi[3] found an exponent 4.4 in the power law of eq 1b, and Osaki and co-workers[4] reported a similar behavior for semidilute PMMA solutions contrary to the expectation from the tube model theory of Doi and Edwards.[5,6] Even older data of Berry and Fox and their proposed theoretical scheme indicate “normal” behavior of PMMA.[7] However, these data and the characteristics of the underlying samples are not well documented.

Plazek[8,9] stated a “unique temperature dependence of the viscoelastic softening” of PMMA that cannot be fitted to a single free-volume expression. Moreover, he found that “one puzzling anomaly is the absence of an entanglement plateau in isotactic PMMA in contrast to very closely spaced entanglements of conventional PMMA (mostly syndiotactic)”.[1,10]

The influence of stereoregularity on the material properties is an important factor that must not be neglected. Very different glass transition temperatures T_g of about 40 °C for 100% isotactic triads and 130 °C for highly syndiotactic PMMA are a striking example. In between, a linear increase of T_g is usually assumed, and for pure syndiotacticity and infinite molecular weight, a value of 160 °C has been extrapolated.[11] Recently, Yasuda et al. have investigated the glass transition temperatures of their monodisperse PMMA samples with chain tacticities from 50 to over 90% syndiotacticity.[12] They have found a smaller dependence on the stereoregularity and extrapolated a T_g of 133 °C.

In the case of PMMA, stereochemistry is easily controlled and determined. With different initiator systems and adjusted reaction conditions, one can obtain a range from 100% isotactic to highly syndiotactic PMMA.[11] To analyze PMMA tacticity, high-resolution proton NMR spectra are conveniently evaluated.[13] Besides, PMMA is miscible with a variety of other polymers and offers the possibility to investigate the influence of different side chains. Up to 1990, indeed, it was difficult or nearly impossible to obtain high molecular weight samples with sufficiently low polydispersity.[14] Only in recent years have these limitations been overcome by living polymerization initiated with aluminum porphyrins,[15] organolanthanide(III) complexes,[12] or lithium alkyls in the presence of lithium salts.[16]

Many findings concerning the rheological properties of PMMA are contradictory and rather confusing in comparison with other polymers. Moreover, judged by its commercial importance, remarkably few rheological data are available for PMMA. Thus, the purpose of the present paper is to reexamine the rheological behavior of well-characterized PMMA samples with different chain tacticities and low polydispersities over a wide range of molecular weights. The experimental data will be compared with existing empirical rules, and the utility of rheological measurements for the accession of a variety of molecular parameters is shown.

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Table 1. Characterization of the Poly(methyl methacrylates)

	SEC				osmometry	static LS	tacticity	T_g (°C)	
sample[a]	M_n (g/mol)	M_w (g/mol)	M_w/M_n	M_z/M_w	M_n (g/mol)	M_w (g/mol)	st, ht, it (%)	10 °C/min	20 °C/min
PMMA40B	41 000	45 000	1.10	1.08	40 000		80, 19, 1		
PMMA45	45 000	46 000	1.03	1.03	44 000		81, 18, 1	132	137
PMMA60	64 000	68 000	1.05	1.04	68 000		81, 18, 1	129	133
PMMA75	65 000	71 000	1.06	1.05	72 000		81, 18, 1	135	135
PMMA110	120 000	135 000	1.06	1.05		155 000	81, 18, 1	134	137
PMMA130	140 000	170 000	1.17	1.11	160 000	190 000	81, 18, 1	130	133
PMMA450	350 000	390 000	1.14	1.09		460 000	81, 18, 1	135	140
PMMA22R	24 000	25 000	1.04	1.04			59, 37, 4	119	121
PMMA62R	58 000	62 000	1.06	1.05			58, 36, 6		
PMMA108R	100 000	108 000	1.08	1.06	100 000		59, 35, 6	121	123
PMMA204R	160 000	200 000	1.26	1.27			43, 47, 10	119	120
PMMA60P	55 000	68 000	1.21	1.16	60 000		74, 23, 3	125	
PMMA100A	50 000	100 000	2.00	2.00			51, 37, 12	116	119

[a] B = provided by BASF AG; R = provided by Röhm GmbH; A = obtained from Aldrich-Chemie (catalog no. 18,224-9); P = polydisperse sample, obtained without LiCl modifier.

Experimental Section

PMMA Samples. Narrow-distribution samples of different molecular weight were prepared by anionic polymerization of MMA in THF at −78 °C. The monomer was previously purified following a methodology involving triethylaluminum.[17] Five samples were synthesized in the presence of a 10-fold excess of LiCl (with respect to *sec*-butyllithium) using an initiator system prepared by the in-situ reaction of *sec*-butyllithium with 1,1-diphenylethylene (DPE).[16,18] For comparison purposes one reaction was carried out with α-methylstyrene instead of DPE (leading to PMMA60), and another without LiCl (PMMA60P; refer to Table 1 for nomenclature).

Four samples (PMMAs are marked with the extension R) having a different tacticity were generously provided by Röhm GmbH, Darmstadt. Three of them were prepared by group transfer polymerization.[19] Because of limitations in this method, the highest molecular weight sample is an anionic standard PMMA (PMMA204R) also obtained from Röhm GmbH.

Finally, PMMA100A is a commercial sample (Aldrich-Chemie catalog no. 18,224-9) prepared by free-radical polymerization containing less than 5 wt % (respectively mol %) of ethyl acrylate.

For characterization and dynamic mechanical measurements, all polymers were redissolved in THF, poured through a membrane filter (pore size 0.45 μm) into methanol, and dried at least 48 h under vacuum at 100 °C. For rheological testing, the sample powders were compression molded at 180 °C under vacuum into 25 mm diameter, completely transparent disks.

Characterization. Molecular weight and polydispersity (designated by the ratio M_w/M_n) were determined by Röhm AG from size exclusion chromatograms (SEC) calibrated with PMMA standards and THF as eluent. Unfortunately, tacticity of the standard samples is not known. Since chain dimensions and hence elution volumes may change with tacticity, the molecular weight values were checked on a HP 502 high-speed membrane osmometer in THF or—for the highest molecular weights—by light scattering on a SLS-modified Sofica instrument. The specific refractive index increment d*n*/d*c* of PMMA450 in chloroform at the wavelength 488 nm was determined to 0.0605 mL/g. Polydispersity was also reexamined in chloroform using our own SEC instrumentation equipped with PL (Polymer Laboratories) gel columns, polystyrene calibration, and a refractive index detector. The values agreed in the range of experimental error and are given without further correction.

^{1}H-NMR (300 MHz) spectra were recorded on a Bruker ARX 300 spectrometer using chloroform-*d* as solvent. The amounts of syndiotactic (st), heterotactic (ht), and isotactic (it) triads were determined by integrating over the peaks at 0.85, 1.02, and 1.21 ppm, respectively.

Glass transition temperatures were read from the middle of the change in the second and third heating curves (rates: 10 and 20 K·min^{-1}) measured on a Perkin-Elmer Model DSC-7 differential scanning calorimeter.

All these physical data of the polymers under study are listed in Table 1.

The first seven samples gathered in Table 1 as series a proved that sterically hindered initiator systems in combination with μ-type ligands such as LiCl are able to produce nearly monodisperse PMMA even without applying the large-scale "break seal" technique.[14] In accordance with Teyssié,[16] these samples are characterized by a high syndiotactic content of 81% independent of the degree of polymerization. Polymerization without LiCl leads to a significantly higher polydispersity and lower stereoregularity, whereas the use of α-methylstyrene instead of DPE had little influence. All SEC traces reveal the typical shape of anionic PMMAs with a sharp decline versus high molecular weights and a small "tailing" toward lower molecular weights. This tailing makes it sometimes difficult to unambiguously fix the integration limits for determining the polydispersity. Apart from this single uniform peak, all SEC measurements gave no hint of any fractions with deviating molecular weight. DSC measurements yield T_gs between 130 and 140 °C for the highly syndiotactic samples, merely dependent on polydispersity and molecular weight. For infinite molecular weight and pure syndiotacticity, we extrapolated a value of about 145 °C, which lies between the two limits of Yuki et al.[11] and Yasuda et al.[12]

Series b—the following four samples in Table 1—consists of samples with less than 59% syndiotactic triads. This special tacticity is nearly identical to so-called "conventional", i.e., radically prepared, PMMA with 59.4% st, 34.6% ht, and 6.0% it.[20] The syndiotactic fraction of our commercial PMMA100A is somewhat smaller, mainly due to the content of ethyl acrylate. T_gs of the conventional samples of about 120 °C are slightly higher than older literature values,[21,22] perhaps as a result of our very narrow molecular weight distribution and the method chosen for determination. For both series, DSC scans up to 220 °C and WAXS measurements provide no indication of crystallinity. This is in agreement with previous studies, where bulk crystallization of PMMA samples with even longer syndiotactic sequences was unsuccessful.[23,24] Formation of stereocomplex is precluded by the low content of isotactic sequences as well.

Dynamic Mechanical Spectroscopy. The dynamic moduli were measured in parallel-plate geometry with a Rheometrics RMS-800 mechanical spectrometer. A distinct heating and measuring procedure (time sweep at a constant frequency of 1 rad·s^{-1}) was used to obtain reproducible frequency sweeps, allowing it to create smooth master curves by time–temperature superposition. As an example, the heating program for PMMA204R performed in the rheometer is given in Figure 1 together with the corresponding changes in the storage modulus. It can be seen that the expected constant moduli are only attained for the two highest temperatures. Nevertheless, on lowering the temperature again, the moduli stayed constant. The increase of the dynamic moduli at the initial temperatures may be attributed to an increasing adhesion of the sample to the plates. This annealing effect was more pronounced for the higher molecular weight samples, and a

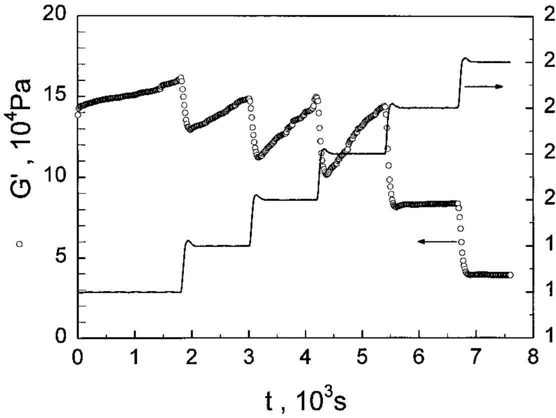

Figure 1. Evolution of the storage modulus *G*′ of sample PMMA204R at constant frequency ($\omega = 1$ rad·s^{-1}) and stepwise increased temperature.

Table 2. WLF Parameters[a]

sample	c_1	c_2 (°C)	c_1c_2 (°C)	T_∞ (°C)
PMMA40B	9.4	175	1646	15
PMMA45	9.4	173	1622	17
PMMA60	9.4	175	1640	15
PMMA75	9.4	176	1656	14
PMMA110	9.4	174	1633	16
PMMA130	9.4	174	1631	16
PMMA450	9.7	175	1706	15
PMMA22R	8.6	177	1517	13
PMMA62R	8.7	174	1514	16
PMMA108R	8.9	176	1563	14
PMMA204R	8.6	180	1550	10
PMMA60P	9.6	181	1739	9
PMMA100A	9.1	195	1772	−5

[a] Reference temperature $T_0 = 190$ °C.

molecular weight of about 500 000 g/mol was found to be a limiting value for reaching the equilibrium state within reasonable periods. Still higher temperatures should be avoided because of decomposition phenomena above 260 °C. We confirmed intact molecular weight distribution after the rheological measurements by SEC.

At the highest temperature, a strain sweep was recorded in order to ensure linear viscoelastic behavior, i.e., strain-independent values of the moduli. Finally, isothermal frequency sweeps were measured from $\omega = 10^2$ to 10^{-2} rad·s^{-1} in the linear viscoelastic region (in general, strain amplitudes are below 12%). Temperatures of the isotherms ranged from 160 to 230 °C for the Röhm PMMAs (series b) and from 170 to 260 °C for the more syndiotactic polymers (series a). The upper temperature limit depended on the molecular weight of the sample.

Results

Within the temperature range 150−260 °C, time−temperature superposition was found to be applicable as expected for linear homopolymers, and the shift factors a_T obey the Williams−Landel−Ferry (WLF) equation:

$$\log a_T = -\frac{c_1(T - T_0)}{c_2 + (T - T_0)} \qquad (2)$$

The shift procedure was performed using a special mathematical algorithm.[25] The WLF parameters c_1 and c_2 as well as the invariants c_1c_2 and $T_\infty = T_0 - c_2$ are given in Table 2. Master curves refer to the reference temperature $T_0 = 190$ °C.

The storage moduli *G*′ as a function of the reduced frequency are presented in Figure 2a for five samples of the series a (polymers PMMA40B and PMMA60 are excluded from the presentation to avoid overlap) and in Figure 2b for the Röhm samples (series b), respectively. Figures 3a and 3b show the corresponding loss moduli *G*″.

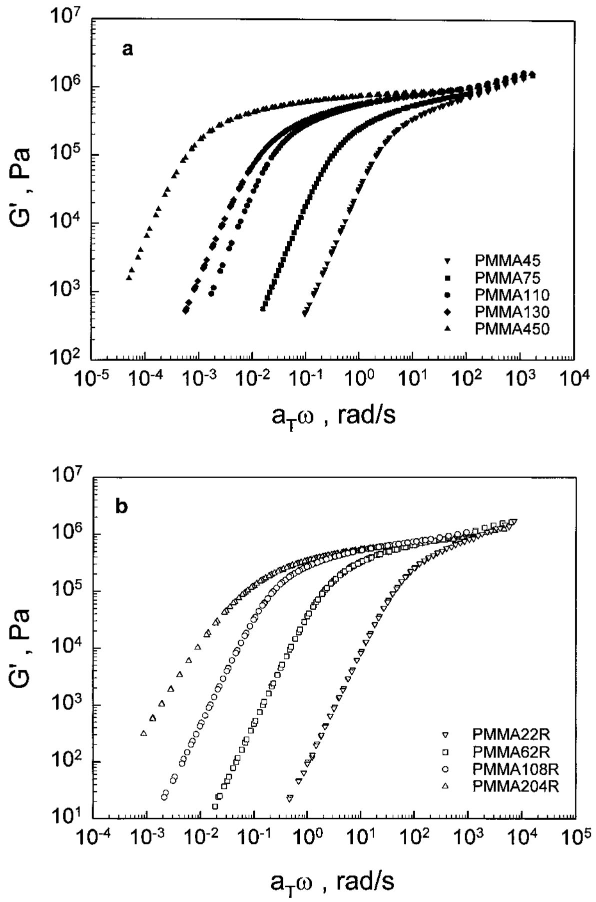

Figure 2. Master curves of the storage moduli *G*′ of the PMMA samples at the reference temperature 190 °C. Note the different frequency scales for the highly syndiotactic samples (series a) in (a) and the conventional samples (series b) in (b).

Zero-shear viscosity and steady-state shear compliance have been calculated from the dynamic moduli in the terminal region according to the following equations:

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \qquad (3)$$

$$J_e^{\,0} = \lim_{\omega \to 0} \frac{G'(\omega)}{G''^2(\omega)} \qquad (4)$$

The obtained material parameters were cross-checked with a Cole−Cole-like plot of ($J'' - 1/\omega\eta_0$) vs J'.[26]

The plateau modulus was determined applying the “tan δ minimum criterion”, i.e., taking G_N^0 equal to the storage modulus *G*′ at the frequency where tan δ is at its minimum in the plateau zone.[27,28]

$$G_N^{\,0} = [G']_{\tan\delta \to \min} \qquad (5)$$

A nonlinear regularization method[29,30] was used to calculate relaxation time spectra $h(\tau)$ from the master curves presented in Figures 2 and 3. The spectrum is calculated on the basis of a regularization algorithm that avoids all difficulties arising from the ill-posedness of this task.[29] It allows the determination of a highly accurate and quasi-continuous spectrum as has been

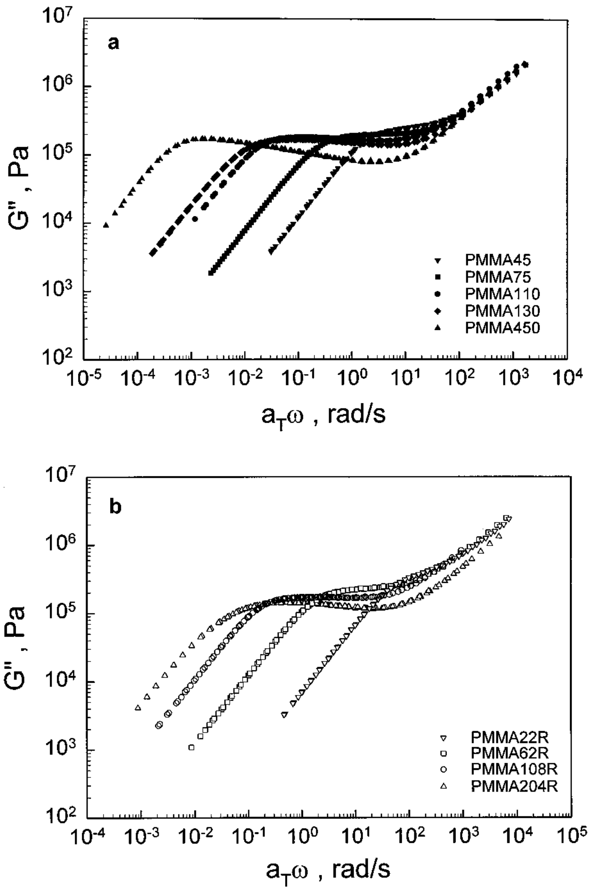

Figure 3. Corresponding to Figure 2, master curves of loss moduli *G*″ of the different PMMAs at 190 °C. Series a is presented in (a) and series b in (b).

proven for a variety of polymers.[31] The spectra are given in Figure 4; part b again displays the relaxation time spectra of the materials with the lower degree of syndiotacticity. The spectra are valid in a range of relaxation times that correspond to $\tau_{\min} = (a_T\omega_{\max})^{-1}$ and $\tau_{\max} = (a_T\omega_{\min})^{-1}$. Two well-expressed maxima exist at the beginning and the end of this range. The location of the maximum at the long-time end is evaluated as the terminal relaxation time τ_0 whereas the maximum at the short-time end maximum will be shown to correspond to the Rouse relaxation time τ_{2x}. These independently determined relaxation times may be compared with values calculated from different material parameters.

Discussion

Thermal Behavior. The shift parameters found might previously be compared at the reference temperature T_0 = 190 °C. In general, the values show good conformity and fall within the ranges known for thermoplastic polymers. No influence of the molecular weight is observed for our samples; this is above 40 000 g/mol for series a and 25 000 g/mol for series b. In contrast, Masuda[3] found c_1 and c_2 of samples below 45 000 g/mol to differ from the values obtained above this molecular weight.

Inspecting a possible influence of tacticity on the WLF parameters, series a and b reveal significantly different averages of c_1: 9.44 for the highly syndiotactic PMMA and 8.70 for the conventional PMMA, respectively. The physical significance of the difference in c_1 may be understood with the concept of free volume.[1] Assuming a linear increase of the fractional free volume with temperature in accordance with the relation

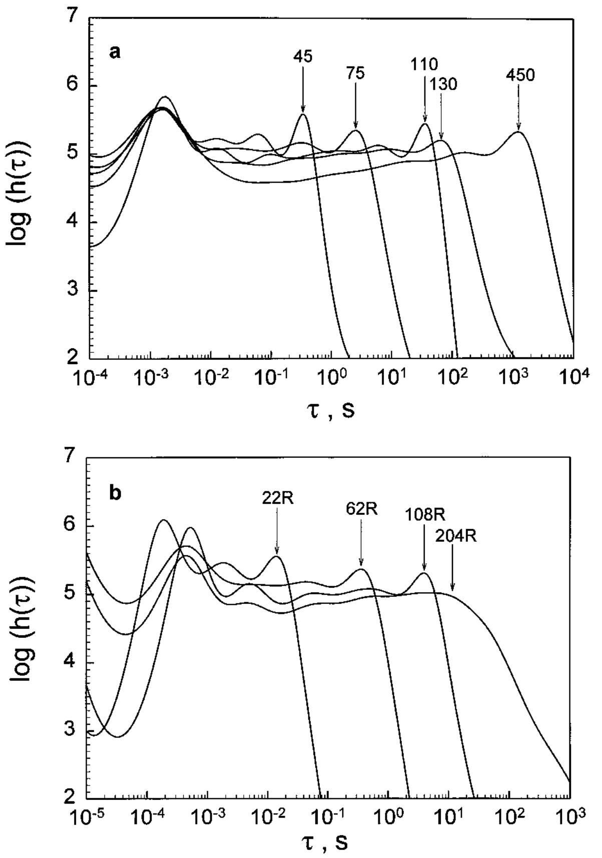

Figure 4. Relaxation time spectra $h(\tau)$ calculated from the master curves displayed in Figures 2 and 3, respectively. (a) corresponds to the highly syndiotactic PMMAs (series a), and (b) to the conventional samples (series b).

$$f = f_0 + \alpha_f(T - T_0) \tag{6}$$

the WLF parameters are identified as

$$c_1 = \frac{B}{2.303 f_0} \tag{7a}$$

and

$$c_2 = f_0/\alpha_f \tag{7b}$$

where f_0 is the fractional free volume at the reference temperature, α_f is the thermal expansion coefficient, and *B* is a constant usually set equal to unity. The smaller value of c_1 for the conventional PMMA then corresponds to larger free volume at the common reference temperature 190 °C and simultaneously reflects the lower T_g of these samples.

It is known that a certain portion of free volume is necessary to achieve chain mobility at the glass transition temperature. Thus, it is now interesting to compare the WLF parameters at T_g as the reference state. From Table 3, the finding that our values of $c_1{}^g$ are the same independent of tacticity agrees with the free volume interpretation.

Still at this point, one might conclude that since the free volume determines the rate of molecular rearrangements and transport phenomena such as diffusion and viscosity, tacticity should exert influence on these parameters. Preliminarily, one can not decide whether it is an intramolecular effect of the chains that leads to a linear decrease of the free volume with the content of

Table 3. WLF Parameters at T_g and Invariants

PMMA sample	T_g (°C)	c_1^g	c_2^g (°C)	c_1c_2 (°C)	T_∞ (°C)	ref
81% syndiotactic	130	14.5	114	1648	15.4	series a
78% syndiotactic	129	11.9	69	821	60	10, 26
conventional (~59% syndiotactic)	117	14.8	104	1536	13.3	series b
conventional	116	21.1	66	1401	50	27
conventional (~55% syndiotactic)	105	20.9	58	1211	47	28
<35% syndiotactic	105	17.0	75	1270	30	8

syndiotactic triads or rather a closer packing in the stereoregular form. We tend to the first explanation, because T_g increases linearly with syndiotactic content and the glass transition is related to the free volume as stated above.

Comparison with other data available for PMMA in the molten state is problematic. Often, no concrete information about tacticity was mentioned and T_g values spread appreciably. Moreover, in our experience the resulting parameters are in practice influenced by the temperature range of the rheological measurements regardless that time−temperature superposition is regularly valid. Thus, we do not want to comment or judge these values quantitatively. In a current cooperation, we intend to include a broader spread in tacticity and *PVT* measurements to investigate the influence of tacticity on the chain flexibility and the free volume more carefully.

Material Functions. The curves presented in Figures 2 and 3 show the well-known behavior of linear, monodisperse polymers: the flow region where $G' \propto \omega^2$ and $G'' \propto \omega^1$ for the lowest frequencies, the plateau region where $G' \propto \omega^\alpha$ (α near to zero) for higher frequencies, and the beginning of the transition region for the highest frequencies. Only in G' of the low molecular weight samples with high syndiotacticity, i.e., PMMA40, PMMA60, and PMMA60P, small deviations from the slope 2 are noticeable. The same anomalies in the terminal flow region are also revealed by the calculated material function J'. We cannot account for this behavior, since torque and storage moduli are still in appropriate regions and the chosen sample preparation should not allow for any cross-linked material. As mentioned above, careful examination of the SEC measurements gave no hints of high molecular traces in any sample. For the present study, the small frequency ranges, where we observed these deviations, were neglected.

The relaxation time spectra of the PMMAs under investigation are given in Figure 4. In general, the spectra are characterized by two large maxima at the long-time and short-time ends as well as by additional maxima and minima between both characteristic times. The intermediate undulations can be traced to experimental scatter. The well-expressed maxima at both ends, however, are still in the experimental frequency range and their magnitude is far beyond being in the order of the error of the spectrum calculation. Thus, the shape of the spectra resembles boxlike spectra as discussed by Ferry.[1] Additionally, Figure 4b allows a comparision between materials of low polydispersity and one material with a significantly higher value of M_w/M_n. A smoother decrease of the intensity toward the longest relaxation times and the loss of the adjoined maximum is observed. In this case, the terminal relaxation time τ_0 was determined from the intersection of two asymptotes.

Another qualitative comparison of samples with nearly the same molecular weight but different polydispersity is given in Figure 5 as the example of the dynamic viscosity vs reduced frequency. It is obvious that the material with the broader distribution reaches the Newtonian plateau at lower frequencies (that corresponds to greater relaxation times) than the sample with higher uniformity. The quantitative influence of polydispersity on different material parameters will be discussed later on.

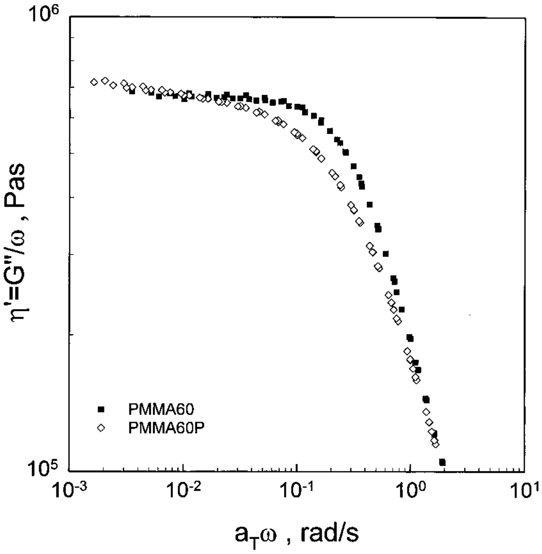

Figure 5. Dynamic viscosity η' vs reduced frequency $a_T\omega$ of two samples (PMMA60 and PMMA60P) with nearly the same molecular weight, but different polydispersity.

Material Parameters. In this section, the dependence of the material parameters like Newtonian viscosity η_0, steady-state shear compliance $J_e°$, plateau modulus $G_N°$, and terminal relaxation time τ_0 on tacticity, molecular weight, and polydispersity will be discussed.

It is well known that for most polymers relation 1 holds true. PMMA was reported as one example that does not follow this viscosity−molecular weight relation due to deviating exponents.[3] Our data presented in Table 4 and Figure 6 imply that PMMA is not an exceptional polymer in this respect. The well-known scaling relation with an exponent a of about 3.4 (3.48 for the more syndiotactic and 3.40 for the other samples) is valid. The exponent of this scaling relation does not depend on tacticity as the difference between both values is not significant.

Clearly detected, however, is a dependence of the viscosity on tacticity in such a way that the prefactor K in eq 1b depends on stereoregularity: the polymers with the higher amounts of syndiotactic triads show a higher viscosity (log $K = -10.8$) in comparison with the polymers of series b (log $K = -11.2$). To check whether this gap between both series disappears if the different glass transition temperatures are taken into account, a comparison at temperatures T_0' equidistant to the T_gs is carried out. Setting the distance of the reference temperature T_0 to the glass transition temperature of series b polymers, $T_{g,b}$, i.e., $\Delta T = T_0 - T_{g,b} = 73$ K, the

Table 4. Material Parameters[a]

sample	$M_w{}^b$ (g/mol)	$G_N{}^\circ$ (Pa)	M_e (g/mol)	η_0 (Pa·s)	$J_e{}^\circ$ (Pa^{-1})	τ_0 (s)	τ_{0n} (s)	τ_{0w} (s)
PMMA40B	44 000	6.30×10^5	7 030	1.07×10^5	2.81×10^{-8}	0.33	0.17	0.30
PMMA45	46 000	6.35×10^5	6 970	1.21×10^5	2.65×10^{-6}	0.342	0.19	0.32
PMMA60	72 000	6.50×10^5	6 810	6.67×10^5	3.21×10^{-6}	2.22	1.03	2.14
PMMA75	76 000	6.75×10^5	6 560	7.80×10^5	3.50×10^{-6}	2.58	1.16	2.73
PMMA110	155 000	7.60×10^5	5 830	9.75×10^6	3.28×10^{-6}	36.2	12.8	32.0
PMMA130	190 000	7.50×10^5	5 900	1.85×10^7	4.45×10^{-6}	65.5	24.7	82.3
PMMA450	460 000	7.60×10^5	5 830	3.70×10^8	4.00×10^{-6}	1260	487	1480
PMMA22R	25 000	6.55×10^5	6 760	6.90×10^3	1.84×10^{-6}	0.014	0.0105	0.0127
PMMA62R	62 000	6.40×10^5	6 920	1.24×10^5	3.05×10^{-6}	0.36	0.19	0.36
PMMA108R	108 000	6.25×10^5	7 090	1.04×10^6	3.90×10^{-6}	3.82	1.66	3.82
PMMA204R	200 000	6.20×10^5	7 140	4.7×10^6	8.0×10^{-6}	25[c]	7.6	27.6
PMMA60P	72 000	6.60×10^5	6 710	6.5×10^5	5.1×10^{-6}	2[c]	1.0	3.3
PMMA100A	100 000	5.75×10^5	7 700	4.0×10^5	4.7×10^{-5}	5[c]	0.7	18.8

[a] Reference temperature T_0 = 190 °C. [b] Weight-average molecular weight deduced from osmotic pressure measurements and polydispersity or—if available—light scattering data. [c] Extrapolated values.

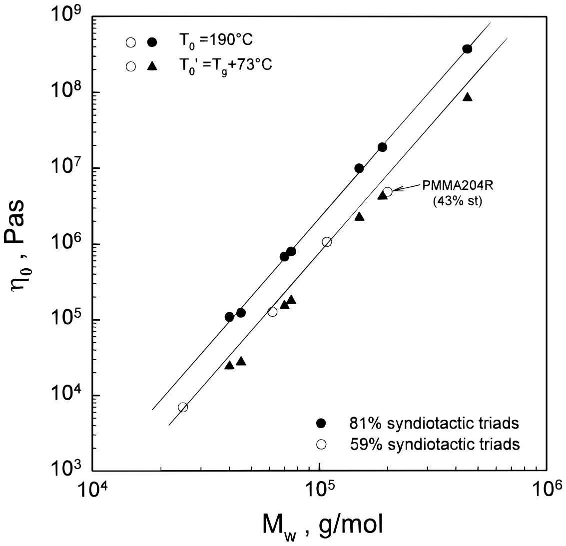

Figure 6. Molecular weight dependence of zero-shear viscosity η_0 for both series with different tacticity at 190 °C. Here, and in the following figures, filled symbols correspond to series a, and hollow symbols to series b, respectively.

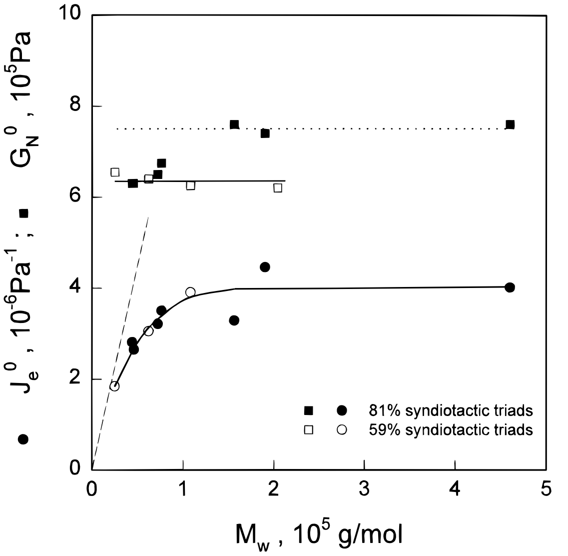

Figure 7. Plateau modulus $G_N{}^\circ$ and the steady-state shear compliance $J_e{}^\circ$ of samples with a polydispersity smaller than 1.15 vs the weight-average molecular weight.

viscosities of series a polymers have to be calculated at $T_0' = T_{g,a} + 73$ °C = 203 °C. The new data determined with the aid of the WLF equation are displayed in Figure 6 by filled triangles. According to this treatment, the new reference temperature T_0' for series b polymers is the same as the old reference temperature T_0, and thus this curve is not shifted. Now, using T_0' as the reference state, the difference between the viscosities of both series is no longer significant. This may be explained on the basis of the free volume concept. Knowing that the free volume at T_g (see eq 7 and Table 3) and thermal expansion coefficient (see ref 33) are independent of tacticity, the same free volume for both series of polymers at the same distance from T_g is the consequence.

Still another possibility to compare the viscosities of the PMMA series is the so-called iso-frictional state, introduced by Berry and Fox.[7] This comparison is carried out at temperatures where the polymers possess the same monomeric friction coefficient, ξ. Selecting $\xi(T_0)$ of the polymers of series b as reference and calculating the temperature at which series a polymers have the same friction coefficient (see p 265 of ref 7) leads to 205 °C. This temperature is very close to T_0' for series a from the comparison at the same distance to the glass transitions. In fact, within the errors of the WLF parameters which are necessary for this calculation, both temperatures are indistinguishable. Thus, in the case of PMMAs with different tacticities, both concepts, the iso-free volume and the iso-frictional state concept, lead to the same result. In principle, it is now possible to calculate the viscosity of a PMMA sample of any known tacticity and molecular weight. Determination of M_c—the crossover molecular weight between both power law regions—was not possible due to missing small molecular weights. We will give an estimate of this value later on using empirical relations.

Another material parameter of great importance is the steady-state shear compliance $J_e{}^\circ$. In Figure 7, $J_e{}^\circ$ values of PMMAs with nonuniformity $M_w/M_n \leq 1.15$ are presented. The experimental data can be described independent of tacticity by the following empirical equation as shown by the full line in Figure 7:

$$J_e{}^\circ = \frac{2}{5}\frac{M_c'}{\rho R T}\left(1 - \exp\left(-\frac{M_w}{M_c'}\right)\right) \tag{8}$$

M_c' is a second critical molecular weight. For small molecular weights, the Rouse behavior seems to be obeyed (dashed line in Figure 7 and eq 9a). For molecular weights much greater than M_c', a molar mass independent plateau is observed. This behavior is well established for other polymers, and eq 8 can be reduced to the known eqs 9:

$$J_e^\circ = \frac{2}{5}\frac{M_w}{\rho RT} \qquad \text{if } M_w < M_c' \tag{9a}$$

$$J_e^\circ = \frac{2}{5}\frac{M_c'}{\rho RT} \qquad \text{if } M_w > M_c' \tag{9b}$$

The intersection of both asymptotes (plateau and Rouse) results in a M_c' value of about 41 000 g/mol. A possible influence of tacticity on this plateau and hence the characteristic molecular weight M_c' is not detectable. Our results conflict with Masuda's finding of a proportionality of J_e° to the molecular weight up to about 340 000 g/mol.[3] He attributed this unusual behavior to the polar groups in the polymer chain of PMMA.

The steady-state shear compliance is known to be sensitive to changes of the molecular weight distribution or polydispersity which can be expressed as the ratio of different moments of the molecular weight distribution. Mills[34,35] derived an empirical relation from data for poly(dimethylsiloxane) and polystyrene, combining the z-average molecular weight M_z and the weight-average molecular weight M_w:

$$J_e^\circ \propto (M_z/M_w)^{3.7} \tag{10}$$

This relationship is depicted in Figure 8. In contrast to Mills, we observed an exponent of about 4.13 independent of tacticity. Other authors reported exponents in the range of 2.5−4.0 or used ratios of different moments of the MWD to describe the correlation between steady-state shear compliance and MWD.[36] Indeed, we could ascertain that in contrast to the viscosity−molecular weight relationship, a greater uncertainty remains about the functional dependence and the exponents. This is due to the greater uncertainty of the experimental data and to missing theoretical justifications.

Commonly, polymers above a critical molecular weight called the entanglement molecular weight M_e reveal a plateau in the G' curve. In general, the corresponding plateau modulus G_N° is found to be independent of the molecular weight. Our plateau modulus data are given in Table 4 and in Figure 7 for series a and b. The filled squares correspond to the syndiotactic PMMAs (series a), the hollow to series b, respectively. The latter show the expected molecular weight independent behavior and an average plateau modulus of 6.35 × 10^5 Pa. In series a, we observe an average value of $G_N^\circ = 7.00 \times 10^5$ Pa ($G_N^\circ = 7.55 \times 10^5$ Pa for the three highest molecular weights) in combination with an unexpected molecular weight dependence. Nevertheless, the mean values are significantly different.

The terminal relaxation times τ_0 of all investigated samples are listed in Table 4. Figure 9 displays the relaxation times of series a (filled circles) and series b (hollow circles) as a function of the molecular weight and indicates the validity of a scaling behavior similar to eq 1:

$$\tau_0 \propto M_w^{\ a} \tag{11}$$

As predicted, the exponent a (3.55 for series a and 3.66 for series b) agrees fairly well with the exponent of the molecular weight dependence of the viscosity. Moreover, the same influence of tacticity is found: the samples with the higher degree of syndiotacticity exhibit longer time constants if compared at the same reference temperature T_0. In Figure 9, the dependence of the terminal relaxation time on tacticity can be removed in the same way as was done for the zero-shear viscosity, i.e., by comparison at the same distance from the glass transition temperature.

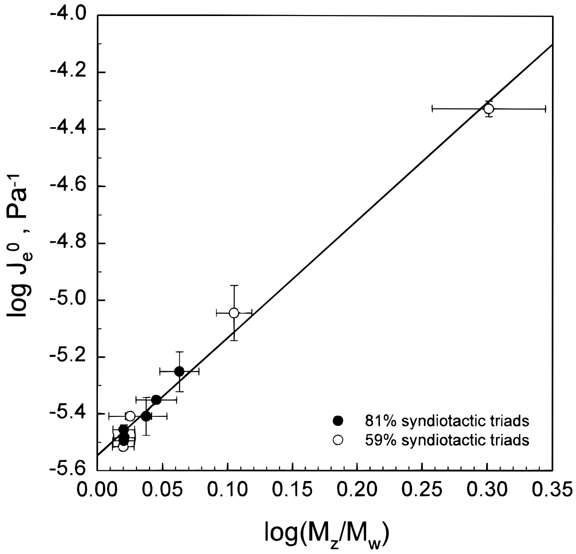

Figure 8. Steady-state shear compliance J_e° vs the polydispersity expressed in terms of the ratio of the z-average and the weight-average molecular weight.

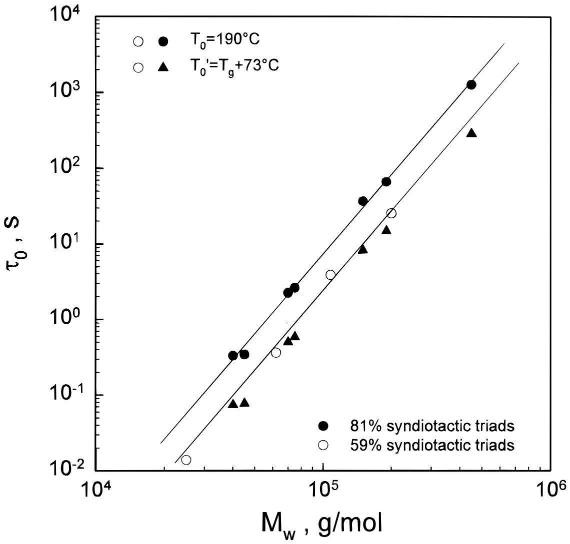

Figure 9. Molecular weight dependence of the terminal relaxation time τ_0 obtained from the long-time maxima of the spectra in Figure 4.

Again, a critical molecular weight that defines a change in the molecular weight dependence cannot be derived from these data. According to Ferry,[1] this critical molecular weight should be the same as for the viscosity, M_c.

Two combinations of viscoelastic constants define the number- and weight-average terminal (longest) relaxation times τ_{0n} and τ_{0w}:

$$\tau_{0n} = \eta_0/G_N^\circ \tag{12a}$$

$$\tau_{0w} = \eta_0 J_e^\circ \tag{12b}$$

The calculated values are given in Table 4 in comparison with the experimental relaxation time τ_0 determined from the spectra. In Figure 9, the calculated data are not included because of the proximity of all three values. Comparison of the different relaxation times reveals that the maximum relaxation time τ_0 from the relaxation time spectrum is nearly identical with the weight-average terminal relaxation time τ_{0w}. Only for polymers with a relatively high polydispersity are deviations noticeable. The number-average terminal relaxation time is approximately half the weight-average time in the case of polymers with low polydispersity. For the polymers with higher polydispersity, the ratio τ_{0w}/τ_{0n}, which can be used as a parameter to characterize the polydispersity, becomes larger.[1] From eqs 12, it is clear that above the critical molecular weights both average relaxation times depend in the same way on the molecular weight as the viscosity.

The characteristic time at the short-time end of the spectra (see Figure 4) was attributed to the Rouse-like relaxation of segments between entanglement points. This is due to the fact that the position of this maximum corresponds to the second crossover frequency, ω_{2x}, between G' and G'' at high frequencies following Ferry's formula: $\omega_{2x} = 8/\pi^2(\tau_{2x})^{-1}$. Ferry himself identified τ_{2x} with the Rouse relaxation time using the entanglement molecular weight instead of the molecular weight of the whole chain. Within each series, this time was found to be independent of the molecular weight. The comparison between both series provides shorter times for series b. Without going into details, this can only be explained by a higher monomeric friction coefficient of the more syndiotactic PMMA in this temperature range.[1] The polymer with the lowest molecular weight in series b shows a shift to even shorter times. This may be a consequence of approaching M_e, at least for fractions of this sample.

Finally, we want to discuss the interrelations between the different critical molecular weights for entanglement coupling. The entanglement molecular weight given in Table 4 has been calculated using the following relation derived from network theories:

$$M_e = \frac{\rho RT}{G_N^\circ} \qquad (13)$$

The obtained entanglement molecular weights fall within the widespread range of literature data for PMMA.[1,27] Our data support a tacticity-dependent M_e. The average entanglement molecular weights of both series are not very different (6400 g/mol for series a and 7000 g/mol for series b) but this difference is significant. Moreover, the different values are in accordance with recently established literature results, i.e., syndiotactic PMMA having smaller coil dimensions and smaller entanglement spacings in comparison with isotactic PMMA.[27]

The critical molecular weights M_c and M_c' are related to the molecular weight between two entanglement coupling loci M_e by the following empirical expression:[1]

$$M_c' \approx 3M_c \approx 6M_e \qquad (14)$$

For many different polymers, this relation has been shown to hold true. On this basis, a calculation of the critical molecular weight M_c yields 12 600 mol/g for polymers of series a and 14 000 g/mol for series b. These results are supported by our data (see Figure 6) in the range of molecular weights at our disposal; no change in the functional dependence can be detected. However, the relation $M_c \approx 2M_e$ could not be proven explicitly due to missing low molecular weight samples of both tacticities.

The calculated critical molecular weight M_c' of 38 400 or 42 000 g/mol agrees fairly well with our experimental point of 41 000 g/mol. Concerning a likely tacticity dependence of M_c', we cannot decide whether this critical molecular weight changes with the degree of syndiotacticity. This is due to the superposed influence of polydispersity on the steady-state shear compliance J_e° and to missing high molecular weight samples with conventional tacticity.

For his anionic PMMAs with 34% syndiotactic triads, Masuda found entanglement spacings M_e between 6800 and 13 000 g/mol, strongly increasing with molecular weight. M_c, however, was estimated to be 30 000–40 000, conflicting with the cited empirical relation. Finally, no critical molecular weight M_c' was accessible, since J_e° was found to be roughly proportional to molecular weight over the complete range. Close inspection of the fractions used in Masuda's study reveals, however, that their polydispersities increase with molecular weight. This could be one reason for the molecular weight proportionality of J_e° up go 340 000 g/mol and the lack of a critical molecular weight M_c' in this case.

Other literature data suffer from insufficient determination of tacticity. As shown above, not only the material parameters are susceptible to varying tacticity but also several relative methods for polymer characterization, e.g., molecular weight determination by intrinsic viscosity or SEC measurements. Thus, these methods only yield correct results if a complete set of PMMAs with the special tacticity of the sample under investigation is used for calibration.

Conclusions

The comparison of experimental data with existing rules like (i) the universal WLF behavior for frequency–temperature superposition, (ii) the scaling behavior for viscosity and terminal relaxation time versus molecular weight, and (iii) the existence of three characteristic molecular weights which fulfill the empirical rule $6M_e \approx 3M_c \approx M_c'$ allows one to judge whether PMMA follows the same behavior as other conventional linear polymers do. For that purpose, the viscoelastic properties of narrow-distribution PMMA were analyzed in terms of tacticity, molar mass, and polydispersity. We found that the frequency–temperature superposition principle is fulfilled and that the shift factors follow the WLF equation. The free volume concept allows an interpretation of the viscoelastic behavior dependent on tacticity.

The dependence of zero-shear viscosity η_0 on molecular weight follows the commonly accepted 3.4 scaling relation. Tacticity of the investigated polymers influences the prefactor: the samples with the higher degree of syndiotactic triads exhibit the higher viscosity. The experimentally determined terminal relaxation time τ_0 follows the same functional relations. The influence of tacticity on both parameters vanishes if they are compared at temperatures equidistant to their glass transition temperatures.

Tacticity also influences the plateau modulus G_N°: the more syndiotactic polymers have a higher plateau modulus. An influence of tacticity on steady-state shear compliance J_e°, however, is not detectable. Here, determining factors are the molecular weight and the polydispersity. The entanglement molecular weight M_e calculated from the plateau modulus is smaller in the case of the more syndiotactic PMMA which yields a tacticity-dependent entanglement molecular weight.

The critical molecular weight M_c' determined from molar mass dependence of the steady-state shear compliance follows the empirical relation $M_c' \approx 6M_e$. Though likely, an influence of tacticity on this critical molecular weight could not be proven.

From all these material parameters, we can state that our syndiotactic PMMA is more entangled and possesses a lower chain mobility and smaller coil dimensions in comparison with conventional PMMA. The glass transition temperature and the corresponding dynamic processes are controlling factors.

The main conclusion of our investigation is that PMMA fulfills the mentioned rules and, therefore, is not an exceptional polymer with respect to its viscoelastic behavior. Previously stated difficulties in understanding the rheological behavior of this polymer may be the consequence of the strong influence of tacticity. Studying this influence, however, can lead to a new understanding of the molecular basis that governs the macroscopic properties of polymers.

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