

## Synthesis and Rheological Characterization of Linear and Star-Shaped Polydimethylsiloxanes

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**SUMMARY:** Linear polydimethylsiloxanes (PDMS) and 3- and 4-arm star-shaped PDMS of narrow molecular weight distribution (MWD) have been synthesized by anionic polymerization. The MWD was obtained by Size Exclusion Chromatography (SEC). Some of the anionically synthesized PDMS showed a relative broad MWD, especially when they were terminated after 3 or more days of reaction. In order to analyze the influence of the extent of reaction on the MWD, a polymerization with sample extractions at different conversions was performed. The MWD of the polymers synthesized at different extents of reaction were studied from a statistical point of view. Linear viscoelastic parameters of the synthesized polymers, such as storage ( $G'$ ) and loss ( $G''$ ) moduli, were obtained at different temperatures as functions of frequency ( $\omega$ ). Zero shear rate viscosity ( $\eta_0$ ) was calculated from the data obtained in the terminal relaxation zone. The molecular weight dependence of  $\eta_0$  shows a good agreement with classical models. Preliminary results obtained from the star polymers suggest an exponential increase in  $\eta_0$  with the number of entanglements per arm.

### Introduction

Anionic polymerization provides an extremely useful tool for the synthesis of macromolecules having a remarkable uniformity of chain length and a predicted molecular weight<sup>1)</sup>. The synthesis involves the successive addition of monomers to growing chains that were previously initiated by reactive species. The addition or propagation step may involve either multiple bonds or ring opening. In the case of polydimethylsiloxane (PDMS), the propagation reaction occurs by ring opening of a cyclosiloxane, which is added to the growing chain. Octamethylcyclotetrasiloxane and hexamethylcyclotrisiloxane are the monomers most commonly used, although others cyclosiloxanes have been reported as monomers for this synthesis<sup>2)</sup>. In a previous work<sup>3)</sup>, we have synthesized linear PDMS with molecular weights ranging from  $2 \times 10^4$  to  $1.2 \times 10^5$ , and polydispersities (*i.e.*  $M_w/M_n$ ) lower than 1.25. Recently, the rheological properties of linear PDMS with higher

molecular weights were reported <sup>4)</sup>. In the present work, we would like to show first some remarkable features on the synthesis of these high molecular weight PDMS. In particular we will describe the influence of the reaction time on the polydispersity of the resulting polymers. We will also present some preliminary results on the rheological properties of linear and star shaped polymers that were prepared. As it is well known, both the size and the molecular architecture of the molecules affect the viscoelastic properties of molten polymers. Several empirical and molecular models have been proposed in the literature in order to explain the existing relationships. The validation of these models requires precise experimental data on well-characterized polymers with narrow molecular weight and pre-determined architecture. When plotted against the weight average molecular weight,  $M_w$ , zero shear rate viscosity measurements for linear polymers clearly show two regions represented as <sup>5,6)</sup>:

$$\eta_0 \propto M_w^a \quad (1)$$

where  $1 \leq a \leq 2.5$  below certain molecular weight, namely the viscosity critical molecular weight,  $M_c$ . The order of  $M_c$  is:  $M_c \cong 2 M_e$ , where  $M_e$  is the average molecular weight between entanglements. For molecular weights above  $M_c$   $a \cong 3.4-3.7$  <sup>6,7)</sup>.

Experimental rheology of long-branched polymers is not as well established. Star-shaped polymers, in which three or more linear polymer chains are connected to a central point of functionality  $f$  by a chemical bond (cross-linking point), are the simplest kind of branched molecules. Theoretical predictions suggest that  $\eta_0$  values for monodisperse star-shaped polymers are lower than those corresponding to monodisperse linear molecules having the same molecular weight. However, the predicted decrease in melt viscosity occurs only for relatively low molecular weight star polymers. At higher molecular weights, the viscosity of star-shaped polymers can be several times higher than that corresponding to linear molecules of the same molecular weight. It has been experimentally observed and theoretically predicted that the viscosity of star-shaped polymers increases exponentially with the number of entanglements in which one arm is involved,  $M_a/M_e$  <sup>7)</sup>. Here,  $M_a$  is the molecular weight of one arm (essentially,  $M_w/f$ ). This behavior can be expressed as <sup>8)</sup>:

$$\eta_0 \propto \left( \frac{M_a}{M_e} \right)^b \exp \left( v' \frac{M_a}{M_e} \right) \quad (2)$$

where the parameter  $b$  can be obtained from different theoretical models and was found to be  $1/2 \leq b \leq 2$  <sup>8)</sup>. When  $b$  is in this range, the parameter  $v'$  is about 0.5-0.6. Viscosity values obtained from eq. (2) are independent on the number of arms of the stars. This behavior was observed in several

polymer systems for  $f \geq 4$ <sup>7-9</sup>. Pearson and Helfand<sup>9</sup> studied 4-arm polybutadiene stars in solution, 4- and 6-arm polyisoprene stars both in solution and bulk, and 4- and 6-arm polystyrene stars in the molten state. Fetters *et al.*<sup>8</sup> reported results on molten polyisoprene stars with 3 to 33 arms.

## Experimental

Linear PDMS with narrow MWD were synthesized by anionic polymerization. The monomer used was hexamethylcyclotrisiloxane (Petrarch Systems, Inc.). The reactions were initiated by *n*-butyl lithium (Alfa Ventron, 2.1 M in hexane) and carried out in glass reactors under vacuum in order to avoid the presence of non-desirable moieties such as H<sub>2</sub>O or O<sub>2</sub>. Previously distilled and dried *n*-hexane and tetrahydrofuran were used as solvent and solvating agent, respectively. Part of the growing chains was terminated in such a way that the resulting polymer contains a reactive vinyl end group (telechelic monofunctional PDMS). For this purpose, vinyltrimethylchlorosilane (Petrarch Systems, Inc.) was used as termination agent. The remainder of the living chains were terminated with tri and tetra-chlorosilanes in order to obtain 3 and 4-arm star-shaped polymers.

The nomenclature utilized for the polymers was the following: those called with LM are linear monofunctional PDMS<sup>4</sup>) and those labeled as S3 or S4 correspond to three and four arm star-shaped PDMS. The number in the star-shaped PDMS name represents the linear precursor polymer (for example, LM11 is the linear precursor (arm) of the star-shaped polymers S3-11 and S4-11).

Star-shaped PDMS were obtained in two ways. Low molecular weight star polymers were prepared by hydrosilation reaction of some of the previously synthesized linear vinyl terminated monofunctional polymers and cross-linking agents with functionality 3 (phenyl *tris*(dimethylsiloxy) silane, Petrarch Systems Inc.) and 4 (*tetrakis*(dimethylsiloxy)silane, Petrarch Systems Inc.). In this case a platinum salt (*cis*-(Pt((C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S)<sub>2</sub>Cl<sub>2</sub>) was used as catalyst. Because of problems with the maximum conversion achieved in this reaction when high molecular weight monofunctional polymers were used, the higher molecular weight stars were synthesized using the living end polymers from the anionic polymerization (LM11 and LM12). Portion of the living polymers were frozen with liquid nitrogen and separated into three parts from the reaction mixture. Each fraction was terminated with different agents. Linear monofunctional (vinyl-ended) PDMS was obtained by adding vinyltrimethylchlorosilane, three and four arm star-shaped polymers were prepared by adding, in several doses, methyltrichlorosilane and tetrachlorosilane (Petrarch Systems Inc.), respectively. In all cases,

the portions of the frozen living polymer was attached to a second glass reactor where the solution was allowed to defrost and reacted with the corresponding termination agent.

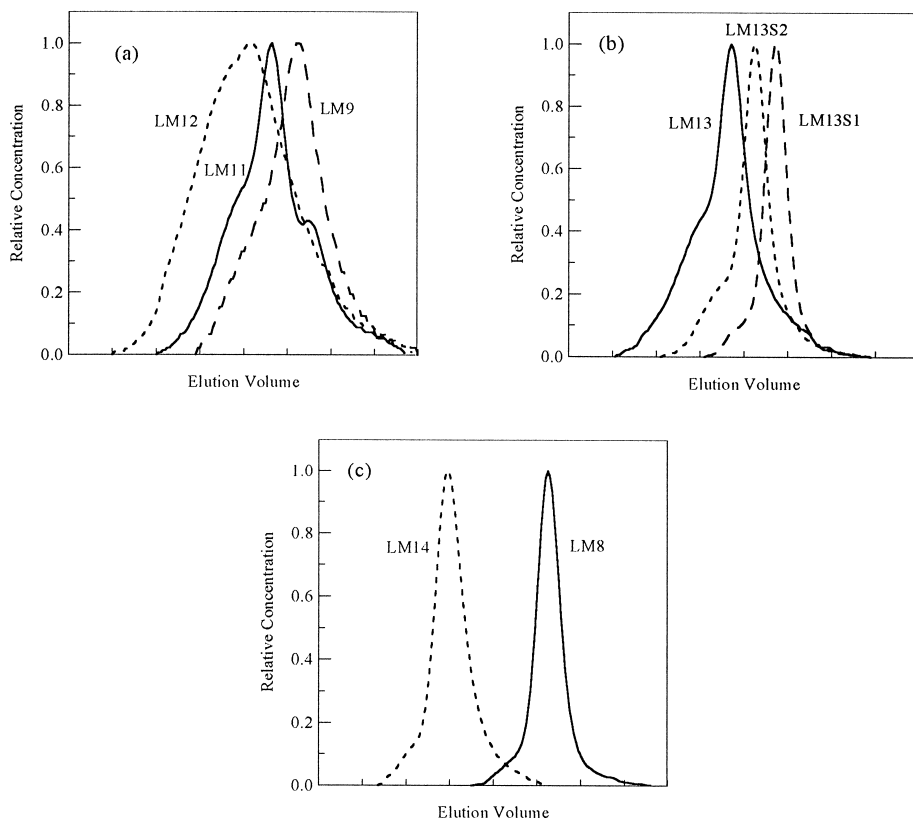
In one of the polymerizations (the one to obtain the polymer LM13), two samples were extracted from the reaction medium at different reaction times (*i.e.*, different extents of reaction). The goal of this reaction was to analyze the effect of the extent of reaction on the MWD of the polymer. The first sample was extracted from the reactor 24 hours after the propagation reaction began. The second extraction was performed after 44 hours from the beginning of the propagation reaction. Finally, the remainder of the polymer was terminated after 72 hours of propagation reaction. The resulting PDMS were labeled LM13S1 (first sample), LM13S2 (second sample) and LM13 (after 72 hours of propagation reaction).

All the synthesized polymers were characterized using Size Exclusion Chromatography (SEC) (Waters Model 440 Liquid Chromatograph) at room temperature. Toluene was used as mobile phase (flow rate = 1 ml/min) and a set of four PL-gel columns ( $500$ ,  $10^3$ ,  $10^4$  and  $10^6$ ) was employed. Number and weight average molecular weights ( $M_n$  and  $M_w$ ) of the linear polymers were obtained by calibrating the SEC with narrow MWD polystyrene (PS) standards (Press Chem. Corp.). Benoit universal calibration<sup>12)</sup> was used and the Mark-Houwink constants for PDMS and PS in toluene at 20°C were obtained from the literature<sup>13)</sup>. The used values were  $K=4.16 \times 10^{-3}$  and  $\alpha=0.788$  for PS and  $K=2.43 \times 10^{-3}$  and  $\alpha=0.84$  for PDMS. The resulting molecular weights were reported in a previous work<sup>4)</sup>. The rheological characterization of the synthesized linear and star-shaped PDMS was carried out in a Rheometrics Dynamic Analyzer RDA-II at temperatures ranging from -40 to 150°C. Shear flow was obtained by dynamical tests using 25 mm diameter parallel plates. Strain-sweep tests at every temperature and several frequencies,  $\omega$ , were performed for the different samples in order to determine the operable strain range to assure linear viscoelasticity. The storage (elastic) modulus,  $G'$ , and the loss (viscous) modulus,  $G''$ , were measured for frequencies ranging from 0.05 to 500 rad/s. Master curves for  $G'$  and  $G''$  were obtained using the time-temperature superposition principle<sup>6)</sup> at 20°C as reference temperature. With this procedure the range of measured frequencies was increased by almost two decades.

## Results and Discussion

Polymers LM9, LM11 and LM12, synthesized at high extents of reaction (> 90%) show a relative broad MWD, as can be seen in Fig. 1a. On the other hand, polymers LM8 and LM14, which were

terminated at lower conversions (40-50%), exhibit a narrow MWD (Fig. 1c). In all the cases that we have studied we found that when the reaction is terminated at conversions of 40-50 %, a polymer with narrow MWD is obtained. This suggests that, at low levels of conversion, the concentration of monomer in the reaction medium is sufficient to allow the inclusion of monomer into the growing chains diminishing the probability of polymer-polymer interaction. At high levels of conversion some kind of redistribution reactions that affect the polydispersity of the chains becomes important. This is explicitly demonstrated in Fig. 1b, which shows the SEC results for the same polymerization of polymer LM13 terminated at 24, 44 and 72 hours of reaction. The broadening of the MWD with reaction time is evident.

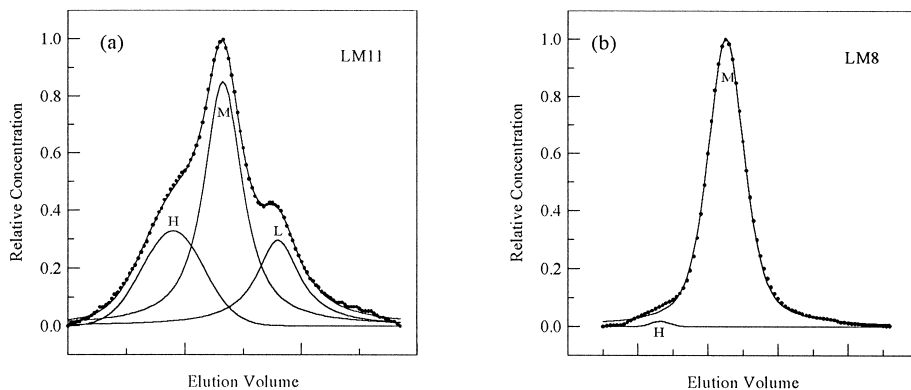


**Figure 1.** SEC chromatograms of the synthesized polymers. a) Polymers obtained after one week of reaction. References: (---) LM9, (—) LM11, and (··) LM12. b) Final polymer and samples obtained in the polymerization with sample extractions. References: (---) LM13S1, (··) LM13S2, and (—) LM13. c) Polymers obtained after 24 h of reaction. References: (—) LM8, and (··) LM14.

In order to investigate the alteration of the MWD, the SEC plots were decomposed in two or three distributions. One of them represents the main narrow peak of the distribution and the others correspond to the higher and lower (when necessary) peaks. To perform the decomposition, statistical symmetric distributions were employed. Mixtures of Gaussian and Lorentzian distributions<sup>14)</sup> provided an adequate option to fit the experimental results. By this procedure, the Gaussian-Lorentzian plots represent the fractions of the main (M), high (H) and low (L) MWD. Therefore, we can estimate the Mw and polydispersity of the molecules that form the tails or the “shoulders” of the whole MWD. Representing the elution volume by  $x$  and the relative concentration of the molecules with elution volume  $x$  by  $f(x)$  in the MWD fits, the Gaussian-Lorentzian distribution can be expressed as:

$$f(x) = \omega_L \left( \frac{A_L}{\pi} \right) \frac{\sigma_L}{(x-m)^2 + \sigma_L^2} + (1-\omega_L) \frac{A_G}{\sigma_G \sqrt{2\pi}} \exp \left( -\frac{1}{2} \frac{(x-m)^2}{\sigma_G^2} \right) \quad (3)$$

where  $m$  is the center of the distribution or mean value ( $f(m)$  is the maximum value of  $f(x)$ ),  $\sigma_i^2$  are the dispersions of  $x$  (for each distribution),  $A_G$  and  $A_L$  are constants and  $\omega_L$ , with  $0 \leq \omega_L \leq 1$ , represents the Lorentzian fraction of the mixture distribution.



**Figure 2.** Experimental (SEC) and Gaussian-Lorentzian distributions for the synthesized polymers a) LM11, and b) LM8. References: (●) Experimental data and (—) Gaussian-Lorentzian fit and H, M and L peaks.

Fig. 2 shows the resulting decompositions (M, H and L distributions) and fits for some of the PDMS synthesized. The polymers terminated after 3 or more days of reaction (LM9, LM11, LM12 and LM13) showed relatively high fractions of chains with higher and lower molecular weights than the mean distribution. On the other hand, the polymers terminated after 24 or 44 hours of reaction only showed a small fraction of high molecular weight molecules.

Table 1. Global fits and peaks of the Gaussian-Lorentzian distributions

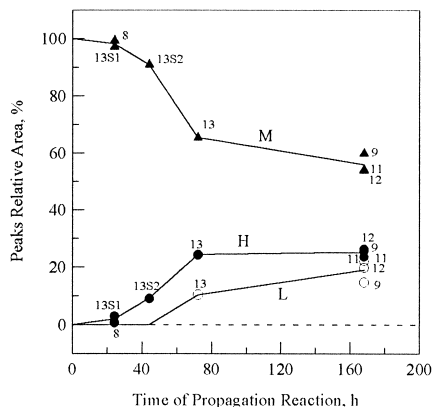
Polymer <sup>a)</sup>	Peak <sup>b)</sup>	Characteristics of the distributions			
		$\omega_L$ (%)	Area (%)	$M_w \times 10^{-3}$	$M_w/M_n$
<b>LM8</b> (24 h reaction) $M_w = 92\ 300$ $M_w/M_n = 1.05$	H	0.5	0.8	155.2	1.02
	M	53.7	99.2	89.3	1.03
	L	---	---	---	---
	Global	---	100.0	91.8	1.05
<b>LM9</b> (7 days reaction) $M_w = 99\ 700$ $M_w/M_n = 1.13$	H	0.01	25.4	136.1	1.03
	M	37.9	59.9	92.9	1.10
	L	51.5	14.7	66.9	1.07
	Global	---	100.0	100.0	1.13
<b>LM11</b> (7 days reaction) $M_w = 168\ 300$ $M_w/M_n = 1.24$	H	0.5	23.6	259.9	1.09
	M	88.5	54.2	161.6	1.13
	L	100.0	22.2	102.9	1.15
	Global	---	100.0	171.8	1.25
<b>LM12</b> (7 days reaction) $M_w = 252\ 900$ $M_w/M_n = 1.47$	H	0.4	26.2	364.7	1.26
	M	0.0	53.9	244.9	1.24
	L	78.1	19.9	127.2	1.32
	Global	---	100.0	252.9	1.44
<b>LM13S1</b> (24 h reaction) $M_w = 141\ 000$ $M_w/M_n = 1.05$	H	0.02	3.0	229.2	1.03
	M	50.8	97.0	138.0	1.06
	L	---	---	---	---
	Global	---	100.0	140.7	1.06
<b>LM13S2</b> (44 h reaction) $M_w = 191\ 200$ $M_w/M_n = 1.12$	H	1.4	9.1	283.3	1.08
	M	82.0	90.9	182.8	1.08
	L	---	---	---	---
	Global	---	100.0	191.9	1.10
<b>LM13</b> (72 h reaction) $M_w = 269\ 400$ $M_w/M_n = 1.20$	H	12.1	24.3	349.4	1.17
	M	98.7	65.4	259.2	1.13
	L	0.03	10.3	158.5	1.19
	Global	---	100.0	270.7	1.21
<b>LM14</b> (24 h reaction) $M_w = 314\ 300$ $M_w/M_n = 1.15$	H	0.9	4.3	478.7	1.14
	M	14.8	73.1	315.6	1.06
	L	100.0	22.6	276.0	1.29
	Global	---	100.0	313.7	1.14

<sup>a)</sup> The  $M_w$  and  $M_w/M_n$  values correspond to SEC characterization

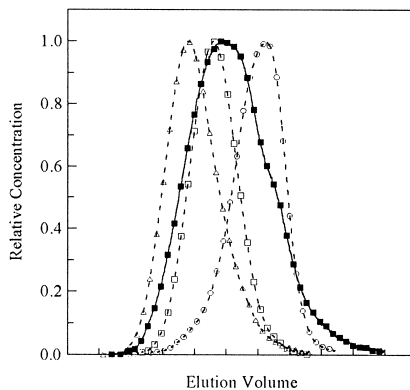
<sup>b)</sup> Global distribution corresponds to the fit of the whole sample (*i.e.*, the sum of the H, M and L distributions)

Table 1 shows the  $M_w$  and polydispersity of the resulting peaks and fits. The Gaussian-Lorentzian fits are simply obtained by the addition of the H, M and L distributions. Fig. 3 shows the evolution of the relative areas of the H and L peaks compared to the M peak as

functions of the propagation reaction time. The H peak appears in all the polymers, but it becomes significant when the time of propagation reaction exceeds 24 hours. The M peak, which is the desired product, represents about 97-99 wt% of the polymer at 24 hours of propagation reaction and decreases as the reaction time grows up. The H and L peaks appear at 24 and 44 hours of propagation, respectively. Then the H fraction increases rapidly up to 72 hours of reaction and then remains practically constant. The area of the L peak slightly increases at a lower rate but steadily, even after one week of propagation (the maximum period that we have studied). Concordantly, the relative area of the main peak presents an important reduction between the first 24-72 hours of reaction and then a more gradual decline. An exception is polymer LM14, which presented an L peak of about 23 wt% although it was terminated at 24 hours of reaction. As this polymer has a relatively high molecular weight, a very low concentration of initiator was utilized in the reaction. Thus, a minimal amount of any impurity is crucial and can affect the initial distribution of the growing chains. Nevertheless, and despite the H and L peaks, the polydispersity of this polymer is reasonably low.



**Figure 3.** Relative peak area (%) for the H (●), M (▲) and L (○) peaks of the Gaussian-Lorentzian distributions vs. time of reaction. Labels references: (8) LM8. (9) LM9. (11) LM11. (12) LM12. (13S1) LM13S1. (13S2) LM13S2. (13) LM13.



**Figure 4.** SEC chromatograms for the polymers S3-11 (■) and the 3 fractions obtained (dashed lines): (△) S3-11F1 (highest molecular weight). (□) S3-11F2. (○) S3-11F3 (lowest molecular weight).

Despite the appearance of H and L peaks, the polydispersity of the M peak of all the polymers terminated at 24 hours of propagation reaction is about 1.04-1.06. On the other hand, at higher reaction times, polydispersity of M peak increases as far as 1.12 to 1.20. The appearance of H and L peaks in the distribution and the increase of polydispersity of the M



peak after 24 hours of propagation reaction suggest that, in order to get molecules with polydispersities below 1.05, the synthesis of PDMS by anionic polymerization must be terminated at that time, when about 40% of conversion is obtained.

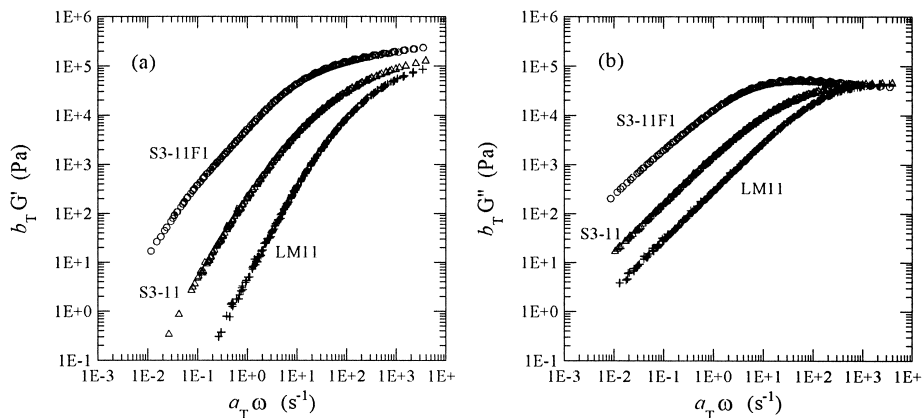
The synthesis of the high molecular weight star PDMS by termination of the living chain resulted in a mixture of linear and star-shaped molecules. This was confirmed by SEC and rheological measurements. In order to obtain pure star molecules, the mixtures were then fractionated into narrow MWD samples (the first of them being the desired 3 or 4-arm star). The fractionation was carried out in a cylindrical column of 17 liters capacity. Successive fractionation<sup>15)</sup> was applied to 20-30 g of crude samples. The solvent used was toluene and the non-solvent was acetonitrile. The solution was stirred continuously and temperature was controlled in order to homogenize the solution. Acetonitrile was added to the polymer-toluene solution until turbidity at 20°C; then the solution was heated until complete transparency (at 30-35°C) and, finally, it was slowly cooled to 20°C. Then, stirring was turned off and after several hours the precipitated polymer was removed from the column. The procedure was repeated with the remaining solution. Fig. 4 shows the chromatograms of the polymer S3-11, obtained from the trifunctional termination of the living chains, and those of the obtained fractions. The first fraction of highest molecular weight is called S3-11F1 and corresponds to the pure stars. The second and third fractions, S3-11F2 and S3-11F3, have molecular weights that verify the following relationship:  $M_{wS3-11F1} : M_{wS3-11F2} : M_{wS3-11F3} = 3 : 2 : 1$ .

The IRIS software<sup>16)</sup> was used in order to construct the master curves at 20°C for  $G'$  and  $G''$  for the linear<sup>4)</sup> and star-shaped polymers. From the time-temperature superposition, two shift factors were obtained<sup>6)</sup>: the frequency shift factor,  $a_T$ , and the modulus shift factor,  $b_T$ . Single master curves of some of the polymers built by plotting  $b_T G'$  and  $b_T G''$  versus  $a_T \omega$  are shown in Fig. 5, which compares  $G'$  and  $G''$  for the non-fractionated polymer S3-11, the first fraction S3-11F1 and the corresponding linear precursor LM11. Zero shear rate viscosity values can be obtained from linear viscoelastic relationships<sup>6)</sup>.  $\eta_0$  as a function of weight average molecular weight for the linear and star-shaped PDMS are shown in Fig. 6. The linear polymers exhibit the two expected regions<sup>6,7)</sup>: the non-entangled region at low molecular weights:

$$M_w \leq 24\,000 \quad \eta_0 = 1.65 \times 10^{-8} M_w^{1.70} \quad (4)$$

and the entangled region at high molecular weights:

$$M_w \geq 32\,000 \quad \eta_0 = 2.48 \times 10^{-16} M_w^{3.47} \quad (5)$$



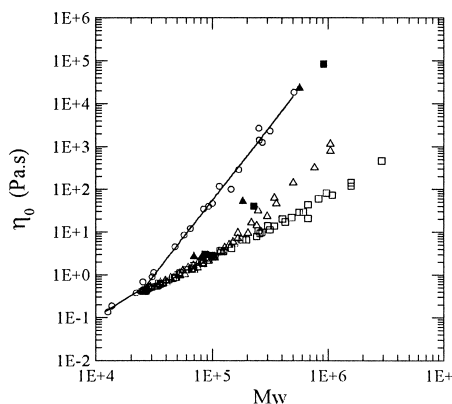
**Figure 5.** a) Elastic modulus ( $b_T G'$ ) and b) loss modulus ( $b_T G''$ ) as a function of frequency ( $a_T \omega$ ) at 20°C for three PDMS: (+) LM11, ( $\Delta$ ) S3-11 and ( $\circ$ ) S3-11F1.

These results from the anionic synthesized polymers were compared those obtained from polydisperse, commercial, PDMS's and other polydisperse siloxanes prepared with an  $A_2 + B_2$  type reaction, by extension of bifunctional polydisperse vinyl terminated linear chains ( $B_2$ ), extended with a bifunctional silane ( $A_2$ )<sup>17</sup>. No substantial difference in the rheological behavior of the narrow MWD, polydisperse commercial and chain extended  $A_2 + B_2$  linear systems was found. The viscosity values of  $A_2 + B_2$  system are not shown in Fig. 6 because they hide the values of the linear synthesized and commercial polymers, but they coincide with the full lines drawn in the plot.

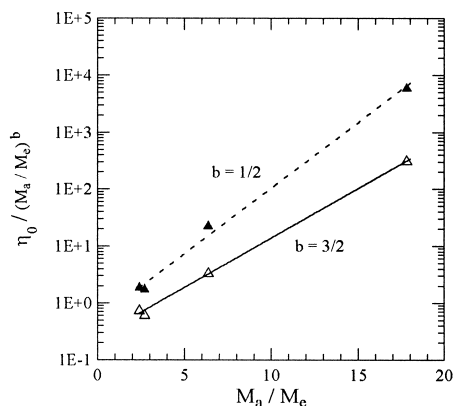
Fig. 6 also compares the  $\eta_0$  values obtained from low molecular weight star-shaped polymers and randomly branched systems with branching functionalities 3 and 4. The randomly branched PDMS were prepared by  $A_3 + B_2$  and  $A_4 + B_2$  reactions where  $A_f$  represents small molecules (silanes) of functionality  $f$ <sup>17</sup>. The lower molecular weight star-shaped polymers present viscosities lower than the linear polymers of identical molecular weight. This is attributed to the smaller radius of gyration of the stars. On the other hand, star PDMS present viscosities higher than those corresponding to random branched systems when they are compared at the same molecular weight. This can be explained by the fact that random branched polymers have a higher number of cross-link points per molecule and, therefore, shorter branches than regular star polymers of similar molecular weight.

Fig. 7 shows preliminary results to test the exponential relationship between  $\eta_0$  and the number of entanglements per arm,  $Ma/Me$ , for the star-shaped polymers (eq. 2). Here, two values of the parameter  $b$  were used: the one proposed by Pearson and Helfand<sup>9</sup>,  $b=1/2$ , and the value

suggested by Fetters *et al.*<sup>8)</sup>,  $b=3/2$ . The parameter  $\nu'$  was found to be 0.53 with  $b=1/2$ , and 0.40 with  $b=3/2$ . These are slightly lower than the values reported for other systems<sup>7-9)</sup>.



**Figure 6.** Zero shear rate viscosity ( $\eta_0$ ) for linear, star-shaped, and randomly branched ( $A_3 + B_2$  and  $A_4 + B_2$ ) systems<sup>17)</sup> as a function of the weight average molecular weight ( $M_w$ ) at 20°C. Symbols: (●) Linear, (▲) 3-arm star-shaped and (■) 4-arm star-shaped PDMS, (△)  $A_3 + B_2$  system and (□)  $A_4 + B_2$  system. Solid line: eqs. (8) and (9).



**Figure 7.**  $\eta_0 / (M_a / M_e)^b$  as a function of the average number of entanglements per arm ( $M_a / M_e$ ) for the 3-arm star-shaped PDMS. Dashed line and filled symbols:  $b = 1/2$ . Solid line and empty symbols:  $b = 3/2$ .

## Conclusions

Linear and star-shaped polydimethylsiloxanes have been synthesized by anionic polymerization. Anionic PDMS synthesized without control of the degree of monomer conversion showed a relative broad MWD. This is due to transfer reactions that seemed to prevail at high conversions. Polymerizations with sample extractions at conversions of approximately 40% and 70% were performed in order to determine the extent of reaction at which transfer reactions become significant. Finally, other polymerizations were terminated at 40-50% of degree of monomer conversion. In this conditions, high molecular weight PDMS with narrow MWD were obtained.

The star-shaped PDMS prepared by multifunctional termination of living chains were contaminated with linear molecules with molecular weights corresponding to the single living chains and their dimers. For this reason, the star polymers were purified by fractional precipitation.

The time-temperature superposition principle was applied to increase the range of frequencies of the viscoelastic measurements. Slopes for  $G'$  and  $G''$  in the terminal relaxation zone are coincident

with the theoretical values<sup>6)</sup> of 2 and 1 respectively and resulted independent on the molecular architecture. At molecular weights below a critical value,  $\eta_0$  for linear polymers increases almost linearly with Mw. On the other hand, for Mw higher than the corresponding critical value,  $\eta_0$  increases with an expected power, according to previous observations<sup>6)</sup>.

In the molecular weight range studied, viscosity values of the low molecular weight star-shaped polydimethylsiloxanes are lower than those corresponding to linear polymers when they are compared at the same Mw. On the other hand, star-shaped molecules showed higher viscosity values than random branched ones. An exponential behavior of the viscosity of the star-shaped PDMS as a function of the number of entanglements per arm was observed, although slightly lower values for the parameter  $\nu'$  were found when compared to other star-shaped polymers systems<sup>7-9)</sup>.

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