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Rheology of Side Chain Dendritic Polymers

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ABSTRACT: We have presented the first rheological studies conducted on a series of side chain dendritic polymers (SCDP) which are produced by copolymerization of dendritic dilos of the second, third, and fourth generation with different semiregid and flexible diisocyanates. The SCDPs, consisting of polyurethane main chain and polyether side chains, obeyed time/temperature superposition. The shift factors as a function of temperature were fitted to the so-called WLF equation. Some results suggested that the dendritic side groups have a distinct effect on the elastic part of the complex modulus, whereas the effect on the viscous part seemed to be small. At low frequencies, SCDPs behaved almost like classical viscous liquids (theory: $G' \sim \omega^2$ and $G'' \sim \omega$; experiment: $G' \sim \omega^{1.5-1.8}$ and $G'' \sim \omega$). At the intermediate frequencies, the experimental exponent was 0.8, which is higher than the theoretical value of 0.5 predicted within the Rouse model. The zero shear viscosities were generated from the low limiting values of $\eta'(\omega)$. For the dendritic macromonomers the viscosity increased with the generation number. For the dendritic polymers, however, the reversed trend was observed; the relative increase of the viscosity upon polymerization is smaller for dendritic polymers of higher generation side groups. These results were discussed in terms of the shielding effect of the dendritic side groups. Furthermore, it was demonstrated that the rheology of the SCDPs can be regulated by the choice of the diisocyanate, i.e., by changing the flexibility of the main chain.

Introduction

Side chain dendritic polymers (SCDP) are a new class of architectural polymers which may display a series of unique characteristics such as direct access to control of the chain conformation and (supra)molecular assembly of the pendent dendritic groups. Although in the literature a number of different synthetic approaches to SCDPs are known,[1] the performance characteristics of this novel type of macromolecules have until now remained largely unexplored. Here we present for the first time the results of research into the rheology of SCDPs. Owing to the special molecular structure of SCDPs, i.e., a flexible main chain jacketed with dendritic side groups of various generations, the rheology of these polymers is expected to differ from the classical behavior observed for linear systems and conventional dendrimers.

Recently, we reported on the synthesis of a new type of architectural dendritic copolymers[2] (see Figure 1). The general synthetic scheme, shown in Figure 1, offers the possibility of producing SCDPs with different degrees of flexibility of the main chain simply by copolymerization of dendritic diols with various diisocyanates. In the previous study we investigated the supramolecular assembly of these SCDPs in both solution and bulk, in addition to the effect of molecular weight on the polymer conformation.[2] Here, we report on the effect of the generation number and flexibility of the main chain on the rheology of SCDPs shown in Figure 1.

Experimental Section

Materials and Synthesis. All the SCDPs were produced in bulk in an oven overnight at 60 °C under a N_2 atmosphere. The polymers were subjected to an additional postcuring treatment (2 h under vacuum at 80 °C). For detailed information regarding materials and synthetic procedure, we refer to the previous publication.[2]

Throughout the text the polymers are designated according to the code Gα-$\beta\beta\beta$, where α is the generation number and $\beta\beta\beta$ is the abbreviation for the type of diisocyanate. In the present study the following diisocyanates have been used: 1,6-hexamethylene diisocyanate (HDI), 1,12-diisocyanatododecane (DID), toluene 2,4-diisocyanate (TDI), and bisphenol F diisocyanate (Bis) (see Figure 1).

Size Exclusion Chromatography (SEC) Experiments. SEC was performed on a Hewlett-Packard chromatograph (HP 1090) equipped with a differential refractometer and differential viscometer detectors placed in parallel (Viscotek 200). The molecular weight values were determined on the basis of the principle of universal calibration[3] using polystyrene standards having known molecular masses ranging from 0.58 to 2800 kg mol^{-1}. To check the applicability of the universal calibration method for the investigated polymers, we compared the results for a few SCDPs with the absolute molecular weight values determined using a light scattering detector (Wyatt Technology DAWN-F DSP) coupled to the SEC equipment. The agreement was quite reasonable. For further information on the experimental conditions for SEC measurements, we refer to the previous report.[2]

Differential Scanning Calorimetry (DSC). The DSC experiments were conducted on a Perkin-Elmer DSC-7 at a rate of 10 °C/min under a N_2 atmosphere. The glass transition temperatures were determined from the first cooling runs.

Rheological Experiments. Viscoelastic behavior of the materials has been investigated using a dynamic stress rheometer DSR200 (Rheometric Scientific). This rheometer is equipped with parallel plates (diameter 25 mm, distance typically 2 mm) which are electrically heated to the testing temperature. The angular frequency can be varied from about 200 rad/s to very low frequencies. The experiments have been conducted under a N_2 atmosphere. The results from the rheometer have been treated by IRIS software for frequency−temperature superposition to produce master curves of the viscoelastic quantities.

Results and Discussion

Characterization of the Molecular Weight. In Table 1, the molecular weight values are given for all

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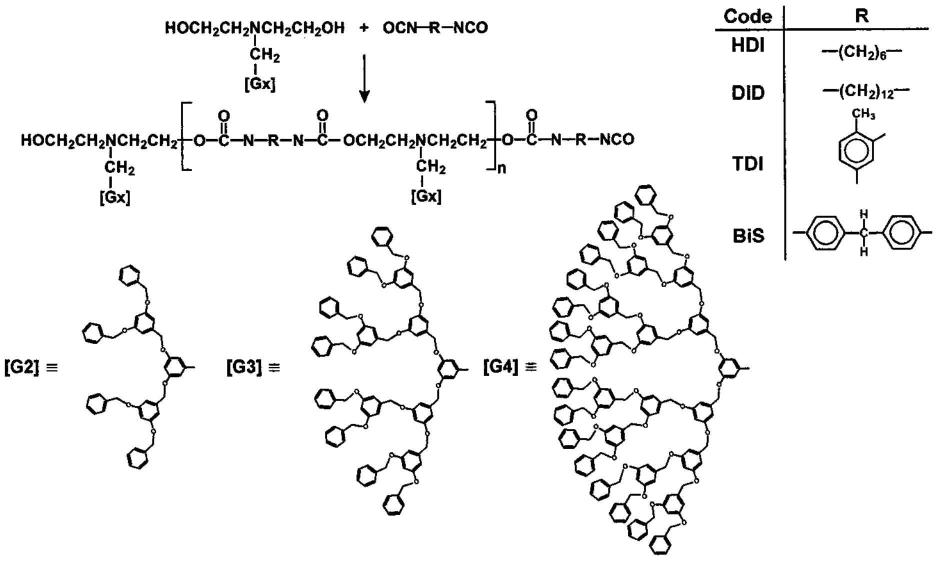

Figure 1. General synthetic scheme used in the present study.

Table 1. Molecular Weight Values of All the Mono- and Polydendrons Determined by SEC Using Universal Calibration[a]

code	M_n	M_w	M_w/M_n	DP[b]	T_g (°C)
G2-N(CH_2CH_2OH)$_2$	770[c]	780	1.0		17.8
G3-N(CH_2CH_2OH)$_2$	1800[c]	1900	1.0		30.8
G4-N(CH_2CH_2OH)$_2$	3300[c]	3300	1.0		37.9
G2-HDI	7200	72000	9.9	8	32.0
G2-DID	7800	149000	19	9	17.5
G2-TDI	14000	38000	2.7	17	50.2
G2-Bis	7100	17000	2.4	9	45.9
G3-HDI	6800	28000	4.1	4	39.2
G3-DID	5600	32000	5.7	3	29.9
G3-TDI	12000	25000	2.0	7	42.6
G3-Bis	14000	26000	1.9	8	42.9
G4-HDI	13000	40000	3.0	4	41.7
G4-DID	32000	88000	2.8	9	39.1
G4-TDI	16000	40000	2.4	5	43.0
G4-Bis	32000	72000	2.3	9	45.9

[a] The molecular weight values are given in g mol^{-1}. The amount of unreacted monomers appeared to be in all cases quite low. [b] The number-average degree of polymerization (DP) is calculated by dividing the M_n values by the theoretical molecular weight values of the monodendrons. [c] These are the experimental data. The theoretical values for G2, G3, and G4 monodendrons are 828, 1680, and 3375, respectively.

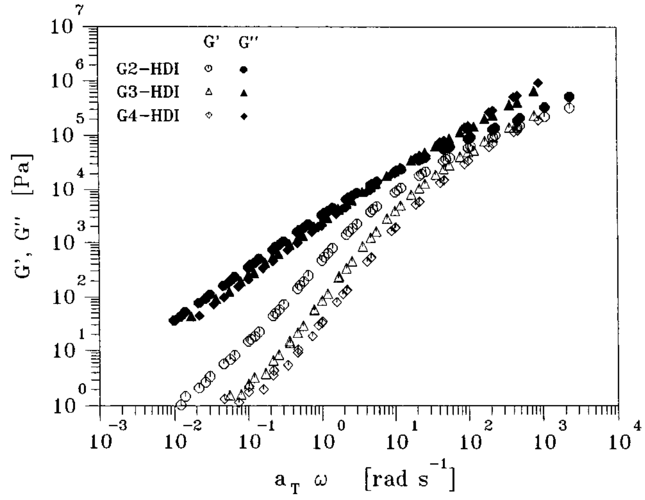

Figure 2. Master curves of storage modulus (G') and loss modulus (G'') versus angular frequency (ω) at the reference temperature T_0 = 80 °C for SCDPs based on HDI.

the polymers investigated here. These values differ somewhat from those presented previously because the SCDPs for this investigation had been subjected to a postcuring treatment in order to remove all the residual solvent.

As can be seen in Table 1, the degree of polymerization is in general rather low. Also, the dendritic polymers, of especially generation two, are quite polydisperse. In the previous report we presented a more detailed interpretation of the molecular weight and intrinsic viscosity values. In the present communication we therefore omit such an analysis and refer to the former study.[2]

Measurements of Storage and Loss Moduli and Application of Time/Temperature Superposition. Figure 2 shows the master curves of storage modulus (G') and loss modulus (G'') as a function of frequency (ω) for SCDPs of various generations based on HDI. The comparison of the visoelastic behavior of SCDPs-based HDI is somewhat difficult because both the degree of polymerization and polydispersity for G2-HDI are higher than those for G3-HDI and G4-HDI (see Table 1). Nevertheless, we believe that the comparison of these data is justified as long as one only indicates the trends observed. The master curves are generated by shifting the data along the ω axis in reference to T_0 = 80 °C. Accordingly the master curves of all SCDPs were created at the reference temperature T_0, which indicates that the empirical principle of time/temperature superposition holds at all the temperatures probed. Although SCDPs consist of chemically different parts, i.e., polyurethane main chain and polyether side chains, they are quite homogeneous systems on the molecular level and display thermorheologically simple behavior. This is somewhat in contrast with the rheology of other types of architectural polymers such as long chain branched polymers, which often have different relaxation times for the side and the main chains.[4]

In general, the shift factors used were roughly identical irrespective of the chemical composition of the SCDPs. We did observe, however, a slight increase of the shift factors for SCDPs of higher generations. The shift factors applied for the three SCDPs, based on HDI, are given in Table 2.

Table 2. Time/Temperature Shift Factors (log a_T) for the Superposition of $G'(\omega)$ and $G''(\omega)$ Curves of SCDPs Based on HDI Measured at Different Temperatures (T_0 = 80 °C)

	log a_T		
temp (°C)	G2-HDI	G3-HDI	G4-HDI
70	0.70	0.89	0.95
80	0	0	0
90	−0.58	−0.59	−0.66
110	−1.52	−1.77	−1.80

Table 3. WLF Fit Parameters of All the Polydendrimers Investigated in the Present Study

code	C^0_1	C^0_2 (K)	C^g_1	C^g_2 (K)
G2-HDI	7.3	115.4	12.6	67.4
G2-DID	8.0	160.7	13.1	98.2
G2-TDI	10.4	107.1	14.4	77.3
G2-Bis	7.4	81.2	12.7	47.1
G3-HDI	7.0	95.3	12.2	54.5
G3-DID	6.0	102.9	11.7	52.8
G3-TDI	8.6	100.0	13.7	62.6
G3-Bis	5.8	63.2	14.0	26.1
G4-HDI	6.5	81.9	12.2	43.6
G4-DID	6.6	95.1	11.6	54.2
G4-TDI	7.1	76.5	13.7	39.5
G4-Bis	7.1	76.5	12.8	42.4

The shift factors as a function of temperature could in all cases be fitted to the so-called WLF equation:[5]

$$\log a_T = -C^0_1(T - T_0)/C^0_2 + T - T_0 \tag{1}$$

where C^0_1 and C^0_2 are fitting constants. The fits were quite reasonable, indicating that the WLF theory may be successfully used to predict the viscoelastic properties of SCDPs. The applicability of the WLF theory to conventional dendrimers has already been demonstrated by Farrington et al.[6] The WLF constants for the present SCDPs are shown in Table 3. To be able to compare the results, the C^0_1 and C^0_2 constants were converted to the values C^g_1 and C^g_2 at the glass transition temperatures (T_g) using the following equations:[4a]

$$C^g_1 = C^0_1 C^0_2/(C^0_2 + T_g - T_0) \tag{2}$$

$$C^g_2 = C^0_2 + T_g - T_0 \tag{3}$$

The fit constants shown in Table 3 are comparable with those found for both linear polymers and classical dendrimers. When comparing the fit parameters of SCDPs based on a certain diisocyanate, it can be seen that, particularly in the case of C^g_2, the values of the fit constants decrease as the size of the dendritic side groups increases, i.e., as the generation number increases. We believe that this is a consequence of the increase of the degree of branching for the SCDPs of higher generations.

As can be seen in Figure 2, $G''(\omega)$ seems to be almost equal for SCDPs based on HDI, whereas $G'(\omega)$ decreases as the generation number increases. Apparently, the size of the side groups does not markedly affect the viscous part of the complex modulus, but it does modify the elastic contribution. This can be attributed to the fact that the extent of intermolecular interactions, such as hydrogen bonding between urethane bonds in the main chain, diminishes as the SCDPs become more shielded by the surrounding dendritic side groups. These results are in close agreement with recent rheological investigations on classical dendrimers, indicating that with increase in generation dendrimers tend to develop from more or less soft, draining molecules toward hard, nondraining spheroids.[7] Because of the dense shell character of classical dendrimers of higher generations, they do not engage in intermolecular interactions and exhibit typical Newtonian flow behavior. Again it should be mentioned that the higher elasticity of G2-HDI may partly have been caused by the higher degree of polymerization and polydispersity.

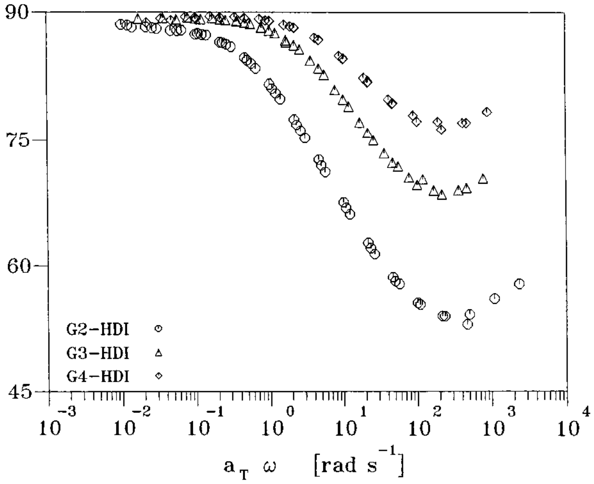

Figure 3. Master curves of loss angle (δ) versus angular frequency (ω) at the reference temperature T_0 = 80 °C for a series of SCDPs based on HDI.

For the samples shown in Figure 2, the variations of G' and G'' at low frequencies are in reasonable agreement with classical laws for viscous liquids ($G' \sim \omega^2$ and $G'' \sim \omega$); the experimentally determined exponent for G'' is around 1.0, and for G' the exponent is between 1.5 and 1.8, depending on the generation number. The somewhat lower exponent values indicate that the systems, at the probed frequencies, still do not behave as a Newtonian liquid. At intermediate frequencies for the SCDP based on G2, we obtained a frequency power law of $G' \sim G'' \sim \omega^{0.5}$, which is in complete accordance with the predictions based on the Rouse theory,[8] where the expected exponent is also 0.5. For SCDPs based on G3 and G4, however, we observed a departure from the Rouse regime; the experimental exponent equals 0.8. Such discrepancies between experimental results and Rouse regime are not unusual. It has been observed for various types of polymers[4a] and theoretically described within the Zimm model, where the hydrodynamic interactions between the beads are taken into account.[9]

Figure 3 shows the master curves of the loss angle for SCDPs based on HDI. As can be seen, the loss angle in all cases goes through a minimum, the absolute value of which depends strongly on the generation number. Apparently the chain relaxation times, before entering the glassy state, become longer for SCDPs of higher generations, which is partly a consequence of the difference in the glass transition temperatures (see Table 1).

The phenomenon of entanglement is fundamental to polymer dynamics. On the basis of the postulated shielding effect of the side chains, we predict that, at least for SCDPs based on HDI, the average molecular weight between two neighboring entanglements (M_e) should increase with the generation number. For the SCDPs studied here we did not observe a rubbery plateau in the $G'(\omega)$, which excludes the existence of

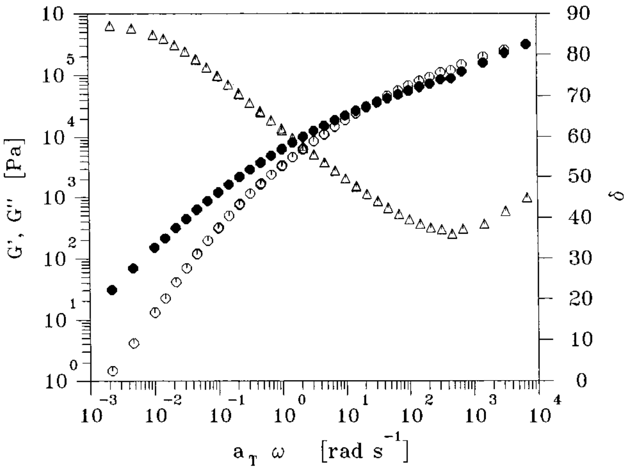

Figure 4. Master curves of storage modulus (*G'*) and loss modulus (*G''*) versus angular frequency (*ω*) at the reference temperature T_0 = 80 °C for dendritic polymer G2-DID.

entanglements. Admittedly, the degree of polymerization of the SCDPs shown in Table 1 is rather low, so that we cannot substantiate the above claim. Further experiments, such as neutron scattering, should reveal the influence of dendritic groups on the backbone rigidity, i.e., persistence length. It must be stated that in one case (G2-DID) the curves of *G'(ω)* and *G''(ω)* did cross, which indicates the formation of some type of temporary network from knots of a finite lifetime (see Figure 4). According to Marvin–Oser theory,[10] M_e can be calculated from the minimum in tan *δ* for a polymer with a narrow molecular weight distribution. For a high disperse polymer such as G2-DID, accurate determination of M_e is not possible.

Analysis of Complex Viscosity. In Figure 5, the complex viscosity data are shown against frequency for all the three dendritic monomers and corresponding SCDPs based on Bis. Fortunately, for these dendritic polymers the degree of polymerization, polydispersity, and T_g are quite comparable, so that the analysis of the viscoelastic behavior is no longer frustrated by such differences in degree of polymerization as observed for the set of polymers used previously. As can be expected, the viscosity of the macromonomers displays a Newtonian flow behavior and increases with the generation number (see Figure 5a). For the corresponding dendritic polymers, however, the trend is different; G3-Bis has the lowest viscosity and G4-B the highest (see Figure 5b). Furthermore, it is clear that SCDP based on G3 shows “shear thinning” already at higher frequencies when compared with G2-Bis and G4-Bis. At first glance, the trend in complex viscosity of dendritic polymers versus generation number seems to be somewhat in conflict with the earlier findings. When considering the relative increase of the viscosity from the macromonomer to dendritic polymer, it can be seen, however, that the viscosity increases upon polymerization with a factor of approximately 20 000 for G2, 2500 for G3, and 1800 for G4. These results provide additional proof for the more effective shielding of the main chain by dendritic side groups of higher generations.

From the low limiting values of *η'(ω)* we have obtained the zero shear viscosity. In Figure 6 these values are plotted against the reduced temperature for the three dendritic macromonomers and corresponding SCDPs-based HDI. For the monomers the zero shear viscosity is highest for G4. For the polymers, however, the opposite trend is observed, which is in agreement with the results shown in Figure 2 and the explanation proposed.

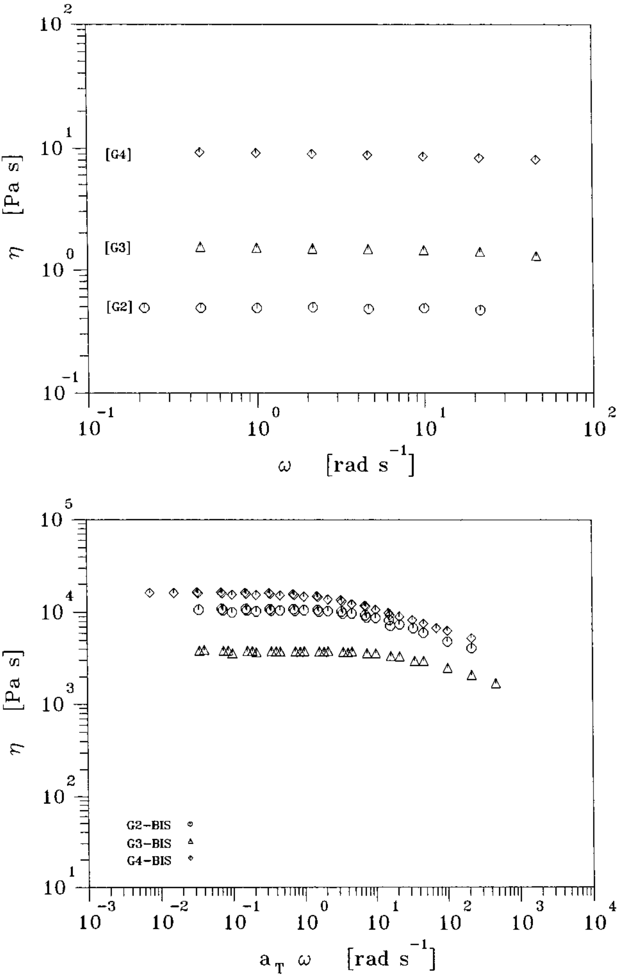

Figure 5. (a, top) Complex viscosity (*η**) versus angular frequency (*ω*) at 80 °C for the monodendrons G2, G3, and G4. (b, bottom) Master curves of complex viscosity (*η**) versus angular frequency (*ω*) at the reference temperature T_0 = 80 °C for SCDPs based on Bis.

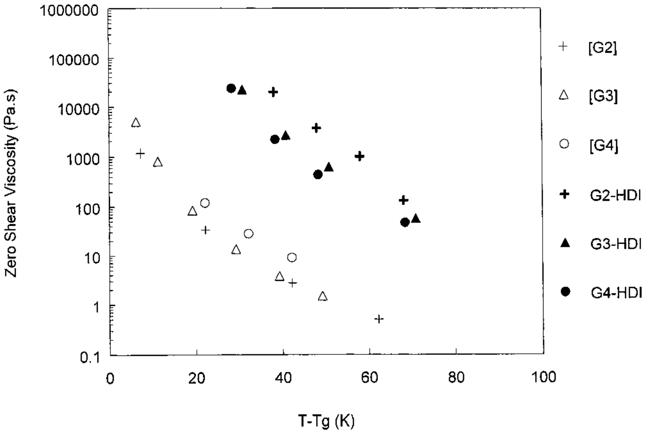

Figure 6. Zero shear viscosity versus reduced temperature ($T - T_g$) for various generation monodendrons and SCDPs based on HDI.

The analysis of the variation of zero shear viscosity with molecular weight provides valuable information regarding the chain conformation and the degree of intermolecular interactions. The zero shear viscosity values for the present SCDPs did not show any clear

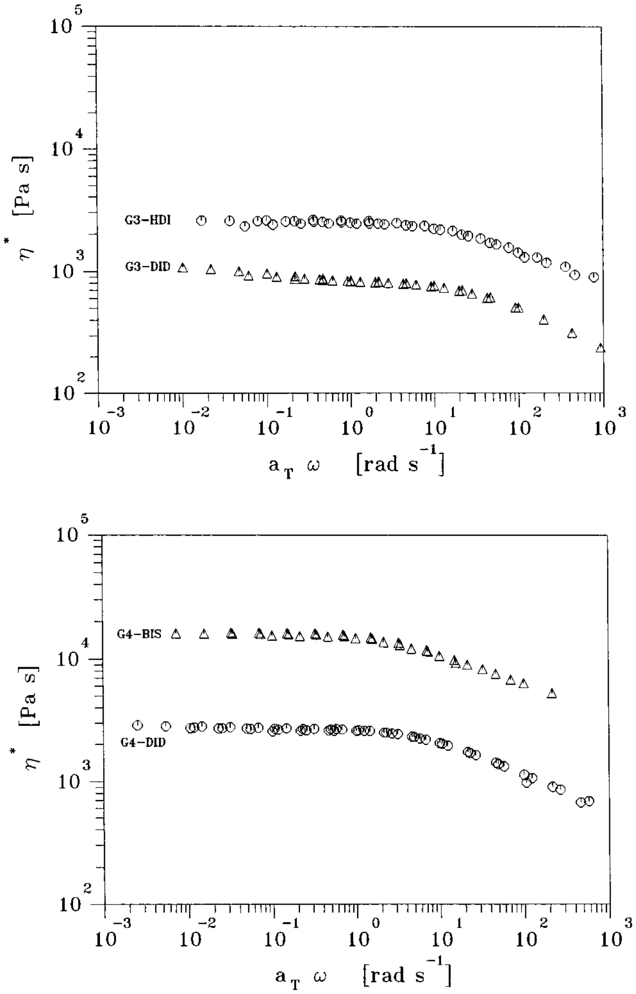

Figure 7. Master curves of complex viscosity (η*) versus angular frequency (ω) at the reference temperature T_0 = 80 °C: (a, top) dendritic polymers G3-HDI and G3-DID; (b, bottom) dendritic polymers G4-Bis and G4-DID.

scaling with the M_w when plotted on a double-logarithmic scale. This could be attributed to the fact that the variation in chemical composition of the main chain often does not allow an unambiguous comparison of the zero shear viscosity data.

Finally, we discuss in short the effect of the main chain's chemical composition on the complex viscosity. Again, the degrees of polymerization and polydispersity for the following SCDPs are quite comparable. In Figure 7, the effect of the main chain's flexibility on the complex viscosity is clearly demonstrated. For both G3 and G4 series, the viscosity of SCDPs based on the most flexible diisocyanate (DID) is the lowest. In Figure 8, the effect of main chain conformation is evident; in comparison with G3-Bis, the complex viscosity of SCDP based on the asymmetric diisocyanate (TDI) is lower and shows Newtonian behavior within a wider frequency range.

Conclusions

Although the present SCDPs have, in general, a low degree of polymerization and a high polydispersity, we have been nevertheless able to draw some qualitative conclusions regarding the rheological behavior of this new class of architectural copolymers. The results presented indicate that the thermorheological behavior of these chemically heterogeneous dendritic polymers is simple and is averaged over the entire macromolecule. Furthermore, there are a number of indications for a nondraining character of dendrimers of higher generations. It seems that these dendritic side groups can shield the polyurethane main chain and prevent it from intermolecular interactions. At the same time, it was shown unequivocally that the rheology of SCDPs can be modified by the choice, i.e., the flexibility, of the diisocyanate which forms the polymer main chain.

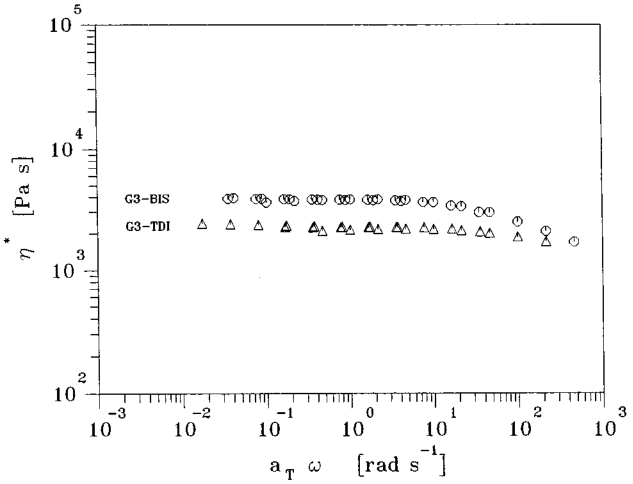

Figure 8. Master curves of complex viscosity (η*) versus angular frequency (ω) at the reference temperature T_0 = 80 °C for dendritic polymers G3-Bis and G3-TDI.

References and Notes

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