e-Polymers **2003**, no. 045.

http://www.e-polymers.org
ISSN 1618-7229

On the entanglement density of differently *N*-substituted alternating styrene-maleimide copolymers

Marcel N. Teerenstra [1], *Paul A. M. Steeman* [2], *Werner Iwens* [1], *Alexander Vandervelden* [1], *Davy R. Suwier* [3,5], *Bruno Van Mele* [4], *Cor E. Koning* [1,3] *

[1] Department of Physical and Colloid Chemistry, Free University of Brussels (VUB), Pleinlaan 2, 1050 Brussels, Belgium

[2] DSM-Research, P.O. Box 18, 6160 MD Geleen, The Netherlands

[3] Department of Polymer Chemistry, Eindhoven University of Technology (TUE), P.O. Box 513, 5600 MB Eindhoven, The Netherlands; Fax +31 40 2463966; c.e.koning@tue.nl

[4] Department of Physical Chemistry and Polymer Science, Free University of Brussels (VUB), Pleinlaan 2, 1050 Brussels, Belgium

[5] Present address: BASF AG, Polymer Research, 67056 Ludwigshafen, Germany

(Received: July 15, 2003; published: September 11, 2003)

Abstract: Differently *N*-substituted maleimides were copolymerized with styrene to yield alternating styrene-maleimide copolymers (SMI-R) with different chain diameters. The polymers were obtained by free radical polymerization and characterized by NMR and size exclusion chromatography / differential viscometry. Glass transition temperatures were measured by differential scanning calorimetry. An increase in chain diameter and chain stiffness is accompanied by a decrease in the entanglement density, reflected in lower values of the plateau modulus, which were corrected for the low molecular weight portion using the Wasserman/Graessley model. Increasing the chain diameter by a factor of two results in a decrease of the entanglement density to one third. SMI-Me showed a much lower entanglement density than polystyrene (PS) although they have the same chain diameter. SMI-Me however is more rigid than PS because of the maleimide five-membered ring structure in the main chain. SMI-Me and SMI-PhOPh show the same glass transition temperature. However, because of the larger chain diameter of SMI-PhOPh, it has a much lower entanglement density. Thus, both the chain flexibility and the chain diameter, two parameters that are strongly related, affect the entanglement density.

Introduction

Entanglement density is one of the main factors influencing the competition between tough and brittle behaviour in amorphous polymers. Entanglements in amorphous polymers refer to the degree of topological constraint on the relative chain motion. In glassy and rubbery states, an amorphous polymer can often be idealized as a network of entangled strands linked at entanglement points. The entanglement network is characterized either by the density of the entanglement points, $\overline{\nu}_e$, or by the average molecular weight of the strands separating neighbouring entanglement points, $\overline{M}_e$.

From the elasticity theory for an ideal rubber it is known that the molecular weight between two crosslinks is inversely proportional to the rubbery plateau modulus. This relation has been successfully adapted to calculate the entanglement density, $\overline{\nu}_e$, for thermoplastic polymers [1-3]. The entanglement density $\overline{\nu}_e$ can be calculated from the experimentally determined plateau modulus at the frequency of minimum damping, G_N°, according to:

$$\overline{\nu}_e = \rho / \overline{M}_e = G_N^\circ / (RT) \qquad (1)$$

where ρ represents the mass density at temperature T at which the plateau modulus G_N° is measured, and R is the gas constant.

The toughness of amorphous polymers seems to depend on the entanglement density rather than on their glass transition temperature, and the entanglement density of polymers is thought to play a determining role in the toughness of polymers by affecting the balance between shear yielding (tough) and craze formation (brittle) (see, e.g., refs. [4-7]). In the literature it has also been postulated that the extremely high toughness of bisphenol-A polycarbonate is also related to main chain motions, enabling the polymer to absorb a large amount of energy before fatal damage occurs [8]. Fetters and coworkers published a couple of papers discussing the relationship between the packing length of a polymer chain, related to the size of the polymer coil and the volume that it occupies, and the plateau modulus. Polymer molecules with a higher packing length proved to have a lower plateau modulus (and accordingly a lower entanglement density) [9,10], irrespective of the nature of the main chain. In effect, the packing length can be related to the molecular diameter of the repeating unit in a polymer chain [11], which latter is the parameter we like to use in the current study. We concentrate on the influence of chain 'thickness' on entanglement density of a series of polymers with an identical main chain. According to earlier work by Wu et al. [1,12], the entanglement density is higher for polymers that contain flexible units. Examples are bisphenol-A polycarbonate, which contains the flexible -O-CO-O- unit, and poly(phenylene ether), which contains the -C-O-C- unit. The average molecular weight between two adjacent entanglements, $\overline{M}_e$, for these intrinsically tough polymers was determined to be relatively low, viz. about 2000 and 3600 g/mol, respectively. These highly entangled materials are extremely tough. Polystyrene and in particular copolymers of styrene and maleic anhydride show rather high $\overline{M}_e$ values in the order of 18 000 - 25 000, so $\overline{\nu}_e$ is low, and in agreement with the above, these materials show a brittle behaviour in the standard impact and tensile tests. These polymers consist of chains that do not fold easily whereas this is a necessity to form entanglements. $\overline{M}_e$ may not only directly depend on the presence of flexible units, but the chain diameter of these chains may play a role as well. In fact, such a relation was found by Wu [13] for a series of poly(alkyl methacrylate)s, but to our knowledge this has never been studied for styrene-maleimide copolymers.

It seems obvious that polymers toughness is related to the chain diameter. Thin chains can form entanglements more easily than chains with a large chain diameter, and as a consequence their entanglement density is expected to be higher. In this paper we study a series of alternating styrene-maleimide copolymers (SMI).

The alternating character of similar polymers has been discussed earlier by Brown et al. [14] They assumed the presence of a styrene-maleimide charge transfer (CT) complex that is radically attacked by the growing chain to give highly alternating polymers. There is also evidence against the participation of a CT complex [15]. Most

likely the truth is in between these extremes: depending on the nature of the monomers, the solvent and the temperature, the equilibrium between CT complex and free monomers shifts [14,16,17]. Other researchers ascribed the alternation to the formation of stabilized transition states at the propagating chain end [18].

We obtained SMI polymers with different chain diameters by using maleimide monomers with different substituents on the nitrogen atom (Fig. 1). The alternating character of the SMI copolymers assures a well defined 'tube diameter'.

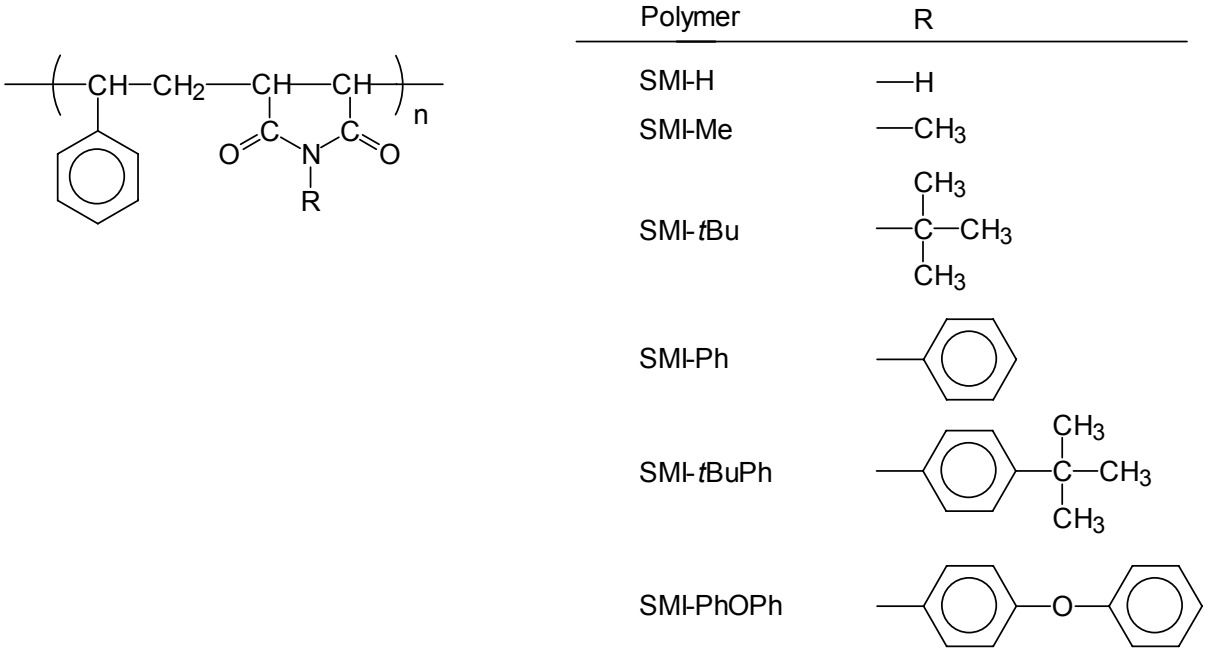

Fig. 1. Structure of the alternating styrene–*N*-substituted maleimide copolymers (SMI)

In earlier work we reported on the relation between the flexibility of the polymer main chain and the entanglement density of flexibilized SMI copolymers. Flexibility was achieved by incorporating poly(tetramethylene oxide) spacers into the main chain, and resulted in an enhanced entanglement density [3,19,20]. In this paper we focus on the relation between chain diameter and chain stiffness on the one hand, and average entanglement density, $\overline{\nu}_e$, on the other hand.

Experimental part

Materials

Styrene (Acros) was distilled under reduced N_2 atmosphere and kept refrigerated until use. Maleic anhydride (Aldrich) was recrystallized from chloroform. Tetrahydrofurane (THF), *N*,*N*-dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) were distilled before use. Maleimide, *N*-methylmaleimide, *N*-*tert*-butylmaleimide and 4-phenoxyaniline (Aldrich) were used without further purification. *N*-Phenylmaleimide (Aldrich) was recrystallized from methanol. 2,2'-Azoisobutyronitril (AIBN, Merck) was recrystallized twice from methanol and kept refrigerated.

Synthesis of monomers

N-(4-*tert*-Butylphenyl)maleimide was synthesized performing a condensation reaction of maleic anhydride and 4-*tert*-butylaniline and a subsequent dehydration to yield the desired monomer [3,21].

N-(4-Phenoxyphenyl)maleimide was synthesized performing a condensation reaction of maleic anhydride (MA) and 4-phenoxyaniline (4PA) using acetic anhydride as dehydrating agent in combination with sodium acetate. MA (19.61 g, 0.20 mol) was dissolved in 250 mL THF and heated to 40°C under nitrogen atmosphere. A solution of 4PA (37.05 g, 0.20 mol) in 150 mL THF was added slowly. After stirring for 20 h we added sodium acetate (4.10 g, 0.05 mol) and finally acetic anhydride (51.05 g, 0.50 mol) as the dehydrating agent. Stirring continued for another 48 h. THF was removed and the reaction product was dissolved in chloroform and subsequently washed with: water, a saturated aqueous solution of $NaHCO_3$, and water. The organic fraction was dried using $MgSO_4$. The solvent was removed under reduced pressure and the crude reaction product was washed with methanol. It appeared that the desired product was insoluble in methanol whereas the side products were soluble. Yield: 71%.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.8 (s, 2H), 7.15 - 7.02 (m, 5H), 7.38 - 7.25 (m, 4H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 118.8 (2C), 119.3 (2C), 123.8 (1C), 125.9 (1C), 127.5 (2C), 129.8 (2C), 134.1 (2C), 156.4 (1C), 156.9 (1C), 169.5 (2C).

$C_{16}H_{11}NO_3$	Calc.	C	72.4	H	4.2	N 5.3
	Found	C	71.7	H	4.3	N 5.4

Synthesis of alternating copolymers of styrene and the different N-substituted maleimides

Copolymers of styrene and the different *N*-substituted maleimides were prepared by a free radical copolymerization using AIBN as the radical initiator and DMF as the solvent. The synthesis of poly(styrene-*co*-*N*-(4-phenoxyphenyl)maleimide) (SMI-PhOPh) (Fig. 1) was performed as follows: *N*-(4-Phenoxyphenyl)maleimide (8.70 g, 32.8 mmol) was dissolved in 40 mL DMF at 70°C under N_2 atmosphere. Styrene (3.42 g, 32.8 mmol) was added and 27.0 mg AIBN (0.25 mol-% with respect to the total monomer concentration) dissolved in 5 mL DMF was added shortly thereafter. The polymerization was carried out for 1 h and 40 min. The polymer solution was precipitated with methanol and the resulting polymer was washed with methanol and dried in vacuum at 80°C. Finally the polymer was dissolved in chloroform (150 mL) and precipitated again using 2.8 L methanol. After filtration, washing and drying, the yield of the resulting polymer was 10.05 g (83%).

Instruments

The number- and weight-average molecular weights (M_n and M_w) as well as the molecular weight distribution were determined using a Waters 2690 Alliance size exclusion chromatograph (SEC) equipped with two Styragel HR 5E columns, a Waters 410 differential refractometer and a Viscotek T50A differential viscometer (DV). The eluent used was THF/acetic acid (95:5 v/v). Absolute molecular weights were calculated by performing universal calibration using polystyrene standards.

Solution viscometry was performed with an Ubbelohde viscometer on 0.8 g/dL solutions in THF at 25°C.

The composition of the copolymers was determined with ^{1}H NMR spectroscopy. The NMR spectra were obtained on approximately 10% (w/v) solutions in chloroform-d_1 ($CDCl_3$) or dimethyl sulfoxide-d_6 (DMSO-d_6). ^{1}H NMR spectra were recorded either on a Bruker AC-250 or AMX-500 spectrometer.

The triad sequence distributions of the SMI-R copolymers were determined using ^{13}C DEPT NMR [22]. These experiments were carried out on the AMX-500 spectrometer.

The second-heating glass transition temperatures were measured on a Perkin Elmer DSC-7 using a heating rate of 10°C/min.

Dynamic mechanical analyses were performed on a Rheometrics RMS 800 mechanical spectrometer equipped with 25 mm parallel plates.

Results and discussion

Molecular characterization

The styrene *N*-substituted maleimide copolymers (SMI-R) (Fig. 1) were prepared from an equimolar monomer feed ratio up to high conversion, using AIBN as the free radical initiator. Using different amines in the monomer synthesis, thereby varying the bulkiness of the substituent on the maleimide nitrogen atom, we obtained copolymers with an identical main chain structure but with a different chain diameter (Fig. 2). Simple molecular modelling showed that the chain diameter of SMI-PhOPh is roughly two times as large as the chain diameter of SMI-H.

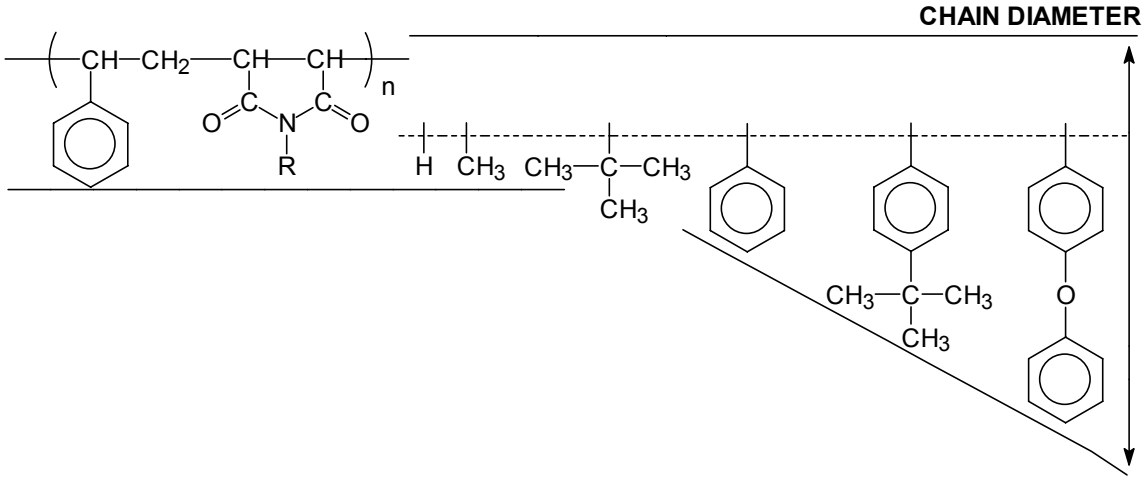

Fig. 2. Schematic representation of the increasing diameter of the chain with larger substituents on the maleimide nitrogen

Results of molecular characterization are summarized in Tab. 1. Intrinsic viscosities, measured with an Ubbelohde type viscometer, correspond quite well to those determined by SEC/DV. The compositions of the synthesized polymers were determined from their ^{1}H NMR spectra and, as expected, the fractions of maleimide were close to 50 mol-% (Tab. 2). It is well known that a nearly alternating structure is

generated when an electron-poor (maleimide) monomer and an electron-rich (styrene) monomer are copolymerized [14].

Tab. 1. Molecular characterization of the SMI copolymers

Polymer	M_n	M_w	$[\eta]_{GPC}$ in dL/g	$[\eta]_{Ubb.}$ in dL/g
SMI-H	133 000	266 000	0.526	0.55
SMI-Me	128 000	344 000	0.457	0.43
SMI-*t*Bu	99 000	203 000	0.550	…
SMI-Ph	146 000	365 000	0.549	0.49
SMI-*t*BuPh	132 000	242 000	0.568	0.55
SMI-PhOPh	159 000	458 000	0.635	0.65

The alternating tendency of the copolymers of styrene (S) and the different substituted maleimides (M) was determined by recording DEPT ^{13}C methylene sub-spectra (Tab. 2). The resonances have been designated as follows: MSM (alternating triad) 32.0 - 37.5 ppm; MSS+SSM (semi-alternating triad) 37.5 - 42.5 ppm; SSS (non-alternating triad) 42.5 - 48.0 ppm [14,22]. We can conclude that predominantly alternating polymers were prepared since the MSM triad accounts for up to 96% of the total amount of triads and in the worst case only 5% SSS triads were found (Tab. 2).

Tab. 2. Composition and microstructure of the SMI-copolymers

Polymer	^1H NMR	^{13}C NMR methylene carbon atom		
	mol-% M	MSM	MSS/SSM	SSS
SMI-H	50	0.83	0.17	0.00
SMI-Me	52	0.94	0.05	0.01
SMI-*t*Bu	53	0.80	0.16	0.04
SMI-Ph	48	0.82	0.13	0.05
SMI-*t*BuPh	48	0.94	0.05	0.01
SMI-PhOPh	49	0.96	0.04	0.00

Thermal characterization

As a result of the incorporation of monomers with a rigid five-membered ring structure into the main chain, the glass transition temperature (T_g) of all six SMI polymers is significantly higher than the T_g of polystyrene. However, there seems to be no correlation between the T_g value and the size of the substituents, probably because the flexibility of the substituent itself influences the T_g as well. The copolymer with the hydrogen substituent, SMI-H, shows the highest T_g of all, most likely due to the fact that this polymer can form hydrogen bonds. The limited rotation in that case is reflected in its high T_g value (Tab. 3).

Tab. 3. Second-heating glass transition temperature, temperature at which the DMA measurements were carried out, Wasserman/Graessley-corrected plateau modulus and entanglement density of the investigated SMI copolymers

Polymer	T_g in °C	T_{DMA} in °C	G_N° in kPa	$\overline{\nu}_e$ in mol/m^3
SMI-H	252	280 - 300	100 ± 25	22 ± 5
SMI-Me	205	250 - 280	100 ± 25	22 ± 5
SMI-*t*Bu	178	220 - 230	100 ± 25	22 ± 5
SMI-Ph	221	280 - 300	100 ± 25	22 ± 5
SMI-*t*BuPh	237	280 - 298	75 ± 20	16 ± 4
SMI-PhOPh	194	240 - 270	30 ± 15	7 ± 3
PS [10,20]	100	190	200	52.0

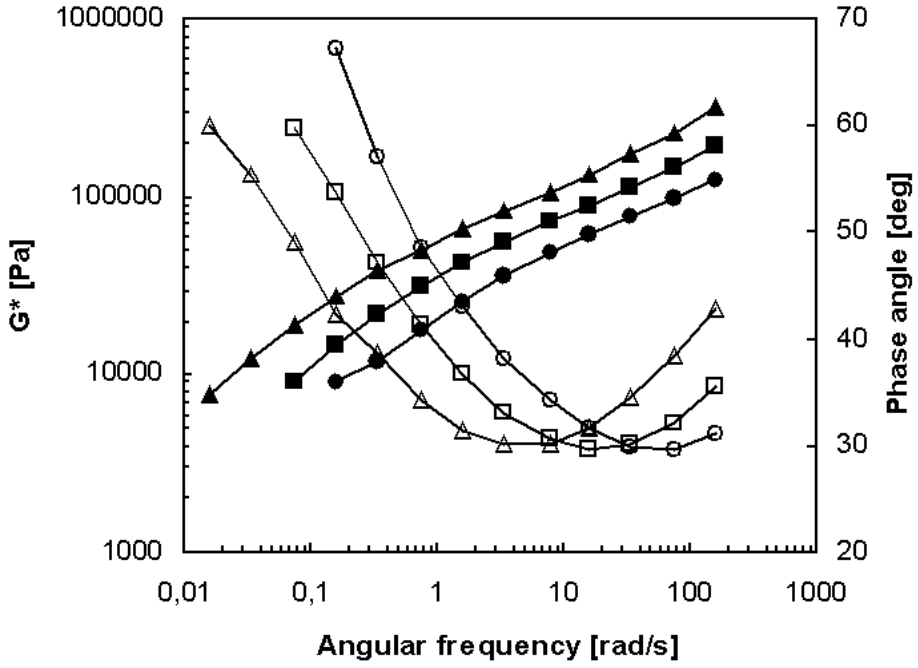

Fig. 3. DMA curves of SMI-Ph at 280°C (Δ), 290°C (□), and 300°C (○). Filled symbols correspond to the dynamic modulus *G**, while open symbols correspond to the phase angle δ

Rheological properties

Fig. 3 shows the results of the dynamic mechanical analysis of SMI-Ph, which serves as a typical example of the dynamic mechanical properties of the SMI-materials. In this figure, the dynamic modulus *G** and the phase angle δ are plotted as functions of the angular frequency ω. Dynamic measurements were performed at 280, 290 and 300°C. These temperatures were selected so that the rubbery plateau, the transition region between glass and flow, is in the experimental frequency window. For none of the materials a well-developed rubbery plateau is found. This is attributed to the insufficiently high molecular weight of the materials in view of their very high

entanglement molecular weights $\overline{M}_e$. However, in all cases a minimum in the phase angle is observed, with phase angle values between 20° and 30°. Following Wu [1] the plateau modulus G_N° has been defined as the dynamic modulus at the frequency of minimum damping.

The ill-developed rubbery plateau of the SMI-materials and the relatively small differences between the plateau moduli urged us to a more in-depth study of possible error sources and consequently the limited reliability of the calculated entanglement densities. From statistical process control measurements we have found that the error in the absolute modulus values we obtain with dynamic mechanical analysis amounts to about ± 5%. The plateau modulus is extracted from the dynamic modulus at the frequency where the phase angle shows a minimum. However, because of the limited number of measurement frequencies per decade, an additional error arises from an inaccurate value of the frequency of the phase angle minimum. For a phase angle of 30° and three measurement frequencies per decade, these errors add up to an error band of ± 15% for the equilibrium modulus.

More importantly, the relatively high values of the phase angle point out that relaxation mechanisms are active at the frequency where the equilibrium modulus is extracted. These mechanisms must be expected to contribute to the dynamic modulus as follows:

1) the low-frequency tail of the glass transition, giving rise to higher modulus values,

2) unentangled/relaxing polymeric chains, diluting the entanglement network and, therefore, giving rise to lower modulus values.

For each of the SMI-materials, given its T_g and molecular weight distribution, both mechanisms may have a significant contribution. In order to get a more quantitative indication of the plateau modulus, the model of Wasserman and Graessley (WG) [23] was used to predict the linear viscoelastic properties of the SMI-melts from their molar mass distributions, as determined with SEC/DV. The dynamic properties were calculated assuming a BSW type relaxation time spectrum [24] for the terminal regime (below 1 rad/s) and a power law for the glass transition regime (above 1 rad/s). Since no relaxation parameters were available for the various SMI types, these were fitted for the best description of the experimental results. Most attention was paid to a good description of the rubbery region. Fig. 4 illustrates a typical example of a model calculation for SMI-Ph. A master curve at 280°C was constructed from the experimental results obtained at 280, 290 and 300°C. The experimental storage modulus G', the loss modulus G'' and the phase angle δ are depicted with symbols. The solid lines are the results of the calculations with the Wasserman/ Graessley model, with optimized relaxation parameters. A good description of the experimental results was obtained. The relaxation parameters were varied around the optimal values, to study their effect on the accuracy of describing the experimental results. It was observed that especially for the equilibrium modulus G_N° only a limited range of values could be used. For SMI-H, SMI-Me, SMI-tBu and SMI-Ph we found a WG-corrected value of 100 ± 25 kPa, which is considerably lower than the value of 200 kPa found for polystyrene [13,25]. For SMI-*t*BuPh and SMI-PhOPh we found significantly lower WG-corrected values (75 ± 20 kPa for SMI-*t*BuPh and an optimal fit at 30 kPa for SMI-PhOPh) (Tab. 3).

From the WG-corrected G_N° values, the corresponding entanglement densities were calculated. All SMI-materials exhibit a marked embrittlement, as compared with pure

polystyrene ($\overline{\nu}_e$ = 52 mol/m^3 [1]). Tab. 3 shows that the entanglement density seriously decreases upon using maleimide comonomers with side groups that significantly exceed the diameter of the styrene units, whereas $\overline{\nu}_e$ does not decrease in case of maleimide monomers with small substituents.

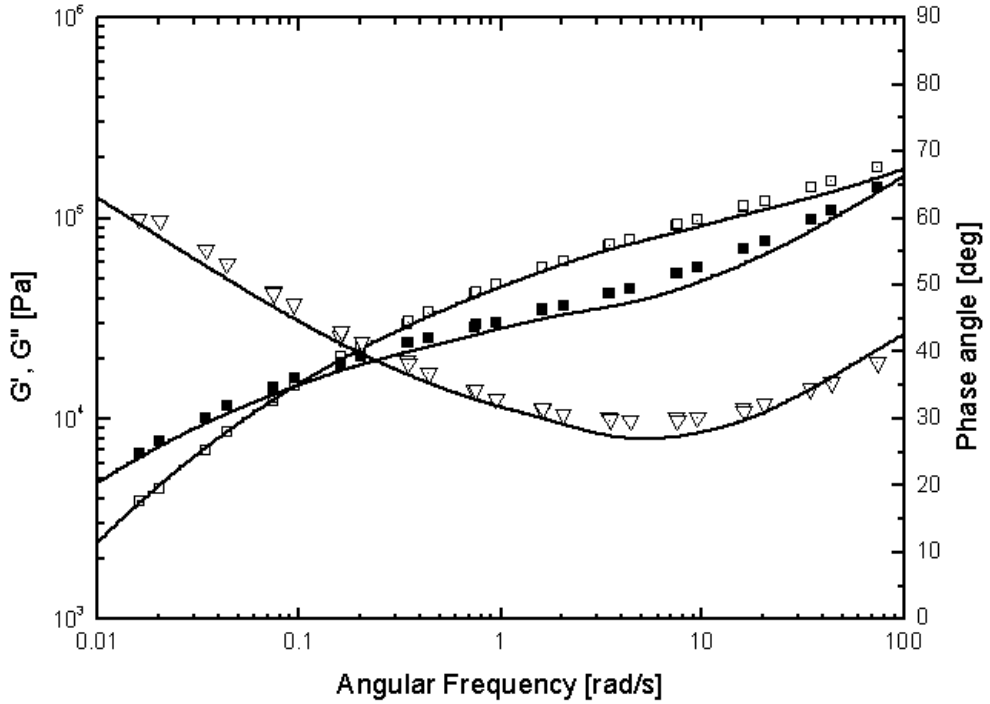

Fig. 4. Experimental and calculated DMA master curves of SMI-Ph at a reference temperature of 280°C. *G*', □; *G*", ■; δ, ∇; solid lines, Wasserman/Graessley model with simulation parameters $\eta_k = 7.0 \cdot 10^{-14}$; a = 3.38, both constants of the monodisperse viscosity relationship. The time scale and the power law coefficient for the glass transition were, respectively, t^* = 0.02 s and β = 0.67

In order to obtain an idea about the relevance of applying the WG model, the plateau modulus G_N°, and from that the entanglement density $\overline{\nu}_e$, were also derived directly from the non-corrected data as presented in Fig. 3, exhibiting the ill-developed rubbery plateau for SMI-Ph. The G_N° value for SMI-Ph as deduced from Fig. 3 is estimated to be 80 - 90 kPa (the WG-corrected value is 100 ± 25 kPa, see Tab. 3), and the corresponding entanglement density is 18 ± 2 mol/m^3 (the WG-corrected value is 22 ± 5 mol/m^3). So, the WG-correction results in a raise of both the plateau modulus and of the entanglement density, although the non-corrected values all fall within the error bars of the WG-corrected data.

In contrast to the T_g there is a correlation between the entanglement density and the size of the substituent (Tab. 3). The small substituents on the maleimide nitrogens, in the case of SMI-H and SMI-Me, stay within the 'tube' formed by the styrene phenyl groups, and hence they do not enlarge the chain diameter. Therefore, the entanglement density is not affected. However, the large substituents, in the case of SMI-tBuPh and SMI-PhOPh, result in a decreased entanglement density, obviously because here the chain diameter is affected. The substituent of the maleimide unit extends further from the backbone than does the phenyl group of the styrene unit

(Fig. 2). Thus, we conclude that the results of model calculations further substantiate our finding that large substituents on the maleimide group, extending beyond the phenyl side group of the styrene co-monomer, viz. *t*BuPh and PhOPh, cause a reduction of the entanglement density because of their effect on the chain diameter. It is observed that an enhanced chain diameter, while keeping the T_g in the same order of magnitude, results in a lower value of $\overline{\nu}_e$ (compare SMI-Me and SMI-PhOPh in Tab. 3). Thus, not only the chain flexibility is important for the entanglement density, but also the chain diameter plays an important role. (Please note that by no means we want to raise the impression that the effect of chain diameter on the one hand and chain stiffness on the other hand can be separated. Of course, these parameters are directly related to one another). What also can be learned from Tab. 3 is that polymers with comparable chain diameters but with a different chain stiffness (compare PS with, e.g., SMI-Me) may exhibit large differences in entanglement density. This shows the importance of choosing a series of polymers with the same main chain structure to study the relation between chain diameter and entanglement density. The resemblance of the data in Fig. 2 and Tab. 3 points to a direct relation between the chain diameter and the entanglement density. Obviously this is valid only if the different polymers of the series contain the same backbone structure.

Finally, we want to devote a few words to the 'packing length' concept, introduced by Fetters and coworkers [9-11] and briefly mentioned in the Introduction of this paper. For a full evaluation of the data of the SMI copolymers according to the packing length concept the average length of a C-C bond in the SMI main chain must be exactly known, and accurate *PVT*-measurements are required, from which the densities of the copolymers, at the respective temperatures at which the plateau moduli have been measured, can be accurately determined. At this moment, these *PVT*-measurements are in progress. However, the packing length itself can be calculated directly from the plateau modulus. Following the procedure described in ref. [9], the packing lengths of the SMI copolymers investigated vary from *c*. 5 - 6 Å for the 'thinner' SMI-H, SMI-Me, SMI-tBu and SMI-Ph copolymers to approximately 6 - 7 Å for the thicker SMI-tBuPh chains, and to *c*. 8 - 9 Å for the SMI copolymer carrying the most bulky side groups, i.e., SMI-PhOPh. For comparison, the packing length of polystyrene is reported to be *c*. 4 Å [9]. It is obvious for this series of SMI copolymers that, in full agreement with Fetter's conclusions, G_N° decreases with increasing packing length, which is caused by the increasing chain diameter [11].

Conclusions

An increase in chain diameter is accompanied by a decrease of the entanglement density, reflected in lower values of the plateau modulus G_N°, which were corrected for the low molecular weight portion using the Wasserman/Graessley model. Increasing the chain diameter by a factor of two results in a decrease of the entanglement density to one third. SMI-Me, which is more rigid than PS because of the maleimide five-membered ring structure in the main chain, showed a much lower entanglement density than PS whereas they have the same chain diameter. On the basis of that observation we can conclude that rigidity affects the entanglement density. On the other hand, SMI-Me and SMI-PhOPh show the same T_g, while SMI-PhOPh has a much lower entanglement density. This result shows that the chain diameter plays an important role too. Thus, both chain flexibility and chain diameter affect the entanglement density.

The T_g does not increase systematically upon the presence of a larger substituent whereas the entanglement density does significantly decrease in the cases where this substituent effectively enlarges the diameter of the chain. On the basis of this work no conclusion can be drawn about the relative impact of the two strongly related parameters chain diameter and chain flexibility on the entanglement density.

Acknowledgement: We would like to express our thanks to Mr. J. Palmen (DMA) of DSM Research Geleen (The Netherlands). This research was financially supported by the Flemish Institution for the Promotion of Scientific-Technological Research in Industry (IWT) and by DSM Research.

[1] Wu, S.; *Polym. Eng. Sci.* **1992**, *32*, 823.

[2] Ferry, J. D.; "*Viscoelastic Properties of Polymers*", 3rd edition, Wiley, New York **1980**.

[3] Teerenstra, M. N.; Suwier, D. R.; Van Mele, B.; Teuwen, L.; Maassen, M.; van den Berg, H. J.; Koning, C. E.; *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3550.

[4] Kramer, E. J.; *Adv. Polym. Sci.* **1983**, *52/53*, 1.

[5] Donald, A. M.; Kramer, E. J.; *Philos. Mag.* **1981**, *43*, 857.

[6] Kramer, E. J.; Berger, L. L.; *Adv. Polym. Sci.* **1990**, *91/92*, 1.

[7] Kramer, E. J.; *Polym. Eng. Sci.* **1984**, *24*, 761.

[8] Xiao, C.; Jho, J. Y.; Yee, A. F.; *Macromolecules* **1994**, *27*, 2761.

[9] Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirke, A.; *Macromolecules* **1994**, *27*, 4639.

[10] Fetters, L. J.; Lohse, D. J.; Milner, S. T.; Graessley, W. W.; *Macromolecules* **1999**, *32*, 6847.

[11] Fetters, L. J.; Lohse, D. J.; Graessley, W. W.; *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1023

[12] Wu, S.; Beckerbauer, R.; *Polymer* **1992**, *33*, 509.

[13] Wu, S.; *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 723.

[14] Brown, P. G.; Fujimori, K.; *Polymer* **1995**, *36*, 1053.

[15] Permentine, G. S.; Jones, S. A.; Tirrell, D. A.; *Macromolecules* **1989**, *22*, 770.

[16] Butler, G. B.; Choon, H. D.; *Makromol. Chem. Suppl.* **1989**, *15*, 93.

[17] Brown, P. G.; Fujimori, K.; Tucker, D. J.; *Polym. Bull.* **1992**, *27*, 543.

[18] Lin, Q.; Talukder, M.; Pittman, C. U.; *J. Polym. Sci., Polym. Chem. Ed.*

1995, *33*, 2375.

[19] Suwier, D. R.; Teerenstra, M. N.; Vanhaecht, B.; Koning, C. E.; *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3558.

[20] Suwier, D. R.; Steeman, P. A. M.; Teerenstra, M. N.; Schellekens, M. A. J.; Vanhaecht, B.; Monteiro, M. J.; Koning, C. E.; *Macromolecules* **2002**, *35*, *6210.*

[21] Sung, P. H.; Chen, C.-Y.; Wu, S.-Y.; Huang, J. Y.; *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2189.

[22] Barron, P. F.; Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. W.; *Macromolecules* **1984**, *17*, 1967.

[23] Wasserman, S. H.; Graessley, W. W.; *J. Rheol.* **1992**, *36*, 543.

[24] Baumgaertel, M.; Schausberger, A.; Winter, H. H.; *Rheol. Acta* **1990**, *29*, 400.

[25] Aharoni, S. M.; *Macromolecules* **1986**, *19*, 426.