Flexibilized Styrene-*N*-Substituted Maleimide Copolymers with Enhanced Entanglement Density

D. R. Suwier,[†,‡] P. A. M. Steeman,[§] M. N. Teerenstra,[||] M. A. J. Schellekens,[†] B. Vanhaecht,[||,⊥] M. J. Monteiro,[†,#] and C. E. Koning*[,†,||]

Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands, and Department of Physical and Colloid Chemistry, Free University of Brussels, Pleinlaan 2, 1050 Brussels, Belgium

Received January 17, 2002; Revised Manuscript Received May 2, 2002

ABSTRACT: High molecular weight poly(styrene-*co*-*N*-substituted-maleimide)-*block*-poly(tetrahydrofuran) multiblock copolymers with an excellent thermal stability were synthesized using the polymeric iniferter technique. Evidence for the existence of these multiblock copolymers was obtained by submitting them to gradient polymer elution chromatography and by snipping the chemical bonds between the SMI blocks and the PTHF blocks, after which the molecular weight distribution of the remaining SMI blocks was determined. Only one glass transition temperature was observed in a modulated temperature DSC scan of the segmented copolymers, typical for a homogeneous material. The T_g of these flexibilized, single-phase multiblock copolymers is still high enough to qualify them as engineering plastics. The entanglement density, which is closely related to the toughness of materials, of a styrene-*N*-phenylmaleimide copolymer flexibilized by 12 wt % PTHF was raised by a factor 1.6 as compared to the unflexibilized styrene-*N*-phenylmaleimide copolymer. These entanglement densities were deduced from the respective rubber plateau moduli, which were corrected for the nonentangled low molar mass fraction by applying the Wasserman−Graessley model.

Introduction

Toughness of a polymer can be considered, to a first approximation, as the work to break under tensile deformation, i.e., the area under the stress−strain curve.[1] In this respect, toughness is related to the deformation of the entanglement network. Information concerning the entanglement network structure in the solid state can be obtained via equilibrium rheological measurements, since the average molecular weight between entanglement nodes, $\bar{M}_{\mathbf{e}}$, can to a first approximation be derived from the rubber plateau modulus in the melt.[2]

It is now well-accepted that the toughness of polymeric materials is related to the degree of entanglement formation of the polymer chains. Wu[3,4] proposed a correlation between the chain stiffness (characteristic ratio C_∞) and the average molecular weight between entanglement nodes, $\bar{M}_e$. Wu's theoretical evaluation and interpretation of the data, however, is highly speculative with respect to the physical reality, especially concerning the assumption of a binary hooking type of entanglement nodes.[5]

More recently, Fetters et al.[6] proposed a more straightforward approach to correlate the entanglement density with the molecular structure of the polymer. They demonstrated that for a large set of data on polymers, there is a very good correlation between the entanglement density ($\bar{\nu}_e$) and a "packing length", p, where p is the actual volume occupied by the chain divided by the square of its end-to-end distance. Wu et al.[3,7] postulated that polymer molecules with a lower characteristic ratio contain more entanglements per unit of volume. Obviously, a certain degree of flexibility is required to form an entanglement. The rule of thumb is that the toughness of polymer materials increases with decreasing $\bar{M}_e$.

In this respect, polystyrene (PS) can be considered as a rather loose network. Its value for $\bar{M}_e$ is approximately 20 kg/mol, and the corresponding entanglement density ($\bar{\nu}_e$) is ca. 52 mol/m^3. On the other hand, bisphenol A polycarbonate (BPA-PC) has $\bar{M}_e$ and $\bar{\nu}_e$ values of approximately 2 kg/mol and 600 mol/m^3,[3] respectively.

Hence, PS is brittle even for high molecular weights, whereas PC is extremely tough.

Copolymers of styrene and *N*-substituted maleimides are extremely brittle, which limits their applications for which toughness is required. Their entanglement density is low and $\bar{M}_e$ is high, i.e., on the order of at least 20 000−30 000 g/mol, depending on the mol % and the type of MI.[8] These polymer chains are rigid and do not bend easily, which is a primary prerequisite for entanglement formation.

In this study we attempt to enable rigid SMI copolymers to form additional entanglements per macromolecule, viz. by "molecular engineering".

Hence, the aim of this work was to enhance the entanglement density of high T_g copolymers of styrene and *N*-substituted maleimides (SMIs) by incorporating flexible poly(tetrahydrofuran) (PTHF) units, homogeneously miscible with SMI, into the rigid SMI main chain. We used the iniferter technique as a tool to synthesize these flexibilized SMI copolymers (see Figure 1).

The iniferter technique is a radical polymerization process discovered by Otsu.[9] The term "iniferter" was given to certain free radical initiators that simulta-

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* Corresponding author.

[†] Eindhoven University of Technology.

[‡] Present address: BASF AG, 67056 Ludwigshafen, Germany.

[§] DSM Research.

[||] Free University of Brussels.

[⊥] Research Assistant of the Fund for Scientific Research−Flanders (Belgium).

[#] Present address: Gradipore Ltd, Frenchs Forest NSW 2086, Australia.

10.1021/ma020084r CCC: $22.00

Figure 1. Schematic representation of the concept of the toughening of a brittle polymer by incorporating flexible main chain segments.

neously undergo chain transfer and polymer radical termination reactions. The various reactions, operative when, for example, a thiuram disulfide is used in a vinyl polymerization, are illustrated in a paper by Nair et al.[10] In this particular type of polymerization, primary radical termination, as well as chain transfer to the initiator, are far more important than bimolecular termination, which is the predominant step in conventional radical polymerizations. Thus, this type of polymerization can be regarded as a repeated insertion of monomer between a disulfide linkage.

In a recent paper we described a polycondensation reaction between diacid-terminated SMI telechelics, which were prepared by the starved feed technique,[11] and dihydroxy-terminated PTHF blocks. However, this technique was restricted to high styrene concentrations.[12] The advantages of the iniferter technique over the earlier described route to synthesize the desired SMI−PTHF multiblock copolymers, viz. a polycondensation reaction, is that by this technique we can synthesize multiblock copolymers that consist of SMI blocks containing a 50/50 mol percentage styrene/maleimide. This will lead to the highest attainable T_g values, which is important for applications at elevated temperatures.

Chain flexibility is not the only parameter that determines the entanglement density. Probably, the diameter of the chain also plays a role, since a thin thread will ply more readily than a thick cable.[8,13] Nevertheless, this study focuses on the flexibility of the chain, and the role of chain diameter has already been discussed in another paper.[8]

In a recent paper[14] we described the synthesis of the PTHF-based polymeric iniferter containing several thiuram disulfide linkages along the chain and the polymerization of styrene and methylmaleimide (50/50 mol/mol) using this iniferter. This resulted in a multiblock copolymer with merely 4 wt % of PTHF and a corresponding limited increase in entanglement density. To raise $\bar{\nu}_e$ to a higher level, SMI−PTHF multiblock copolymers with a higher PTHF content are required, still exhibiting a homogeneous character. Their synthesis and characterization are described in this paper. Furthermore, it is attempted to estimate the relative toughness of the single-phase multiblock polymers by determining the entanglement density ($\bar{\nu}_e$) by dynamic mechanical analysis, and comparing the obtained value with the $\bar{\nu}_e$ of a nonflexibilized SMI reference copolymer.

These flexibilized SMI copolymers, with an expected increased toughness, would be more useful in engineering plastics applications than their nonflexibilized counterparts.

Experimental Section

Materials. Styrene (Acros) was distilled under reduced N_2 atmosphere and kept refrigerated until use. *N*-Phenylmaleimide (Aldrich) was recrystallized from a methanol/water mixture. Thionyl chloride, piperazine, trimethylamine, DMF, *N*-methylmaleimide (Aldrich), carbon disulfide (Merck), iodine (Acros), tetrahydrofuran (Biosolve), and hydroxy-terminated poly(tetrahydrofuran) (PTHF, $\bar{M}_n = 1000$, Polysciences) were used without further purification. Triethylamine (Aldrich) was distilled from $MgSO_4$. Chloroform was distilled and dried on molecular sieves.

Table 1. Amounts of Styrene, Maleimide, PTHF-1000-Based Iniferter, and Solvent Utilized in the Synthesis of (SMI-*block*-PTHF)$_n$ Multiblock Copolymers

entry	styrene (g) [mmol]	maleimide used (g) [mmol]	polymeric iniferter (g) [mmol]	wt % PTHF	solvent DMF (mL)
1	10 [96.2]	methylmaleimide 10.7 [96.2]	0.5 [0.04]	2	40
2	10 [96.2]	phenylmaleimide 16.6 [96.2]	3.0 [0.22]	10	50

Synthesis of the Polymeric Iniferter Based on Hydroxy-Terminated PTHF ($\bar{M}_n = 1000$ g/mol). The synthesis of the polymeric iniferter was carried out by following a description by Clouet.[15] Exactly the same procedures and amounts of reagents were used as specified in the literature.[16] The characterization was done by elemental and spectral analyses, as well as by size exclusion chromatography with on-line intrinsic viscosity measurement (SEC/DV).

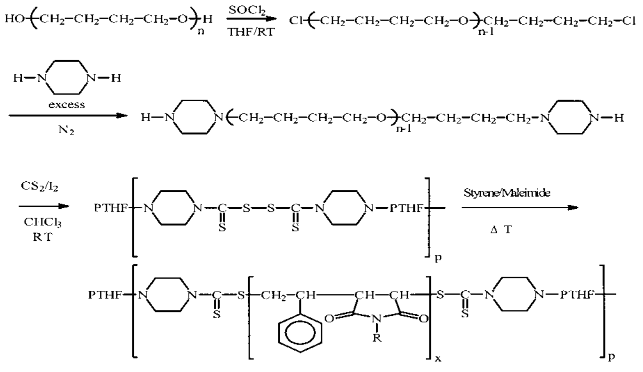
Synthesis of Segmented Copolymers. Polymerizations were performed in sealed evacuated glass tubes wrapped in aluminum foil. The tube containing the monomers styrene and *N*-methylmaleimide or *N*-phenylmaleimide, the polymeric PTHF-based iniferter, and dimethylformamide (DMF) was deaerated by several cycles of freezing and thawing and then sealed under vacuum. The exact amounts of chemicals used are shown in Table 1. The polymerization was carried out in an electrically controlled thermostatic oil bath at 120 °C, during 1 day. After the polymerization, the content was precipitated into methanol, redissolved in chloroform, reprecipitated in methanol, and dried in a vacuum at 100 °C. The polymers were characterized by ^{1}H NMR[14] (6−7 ppm, aromatic protons of the phenyl unit; 1−5 ppm, protons of the backbone; 3.4 ppm, CH_2OCH_2 protons of the PTHF blocks; 2.8 ppm, CH_3 protons if the maleimide substituent is a methyl group; 1.6 ppm, CH_2–CH_2 protons of the PTHF blocks), SEC/DV, TGA (thermogravimetrical analysis), MDSC (modulated temperature differential scanning calorimetry), and DMA (dynamic mechanical analysis).

Snipping of the SMI−PTHF Multiblock Copolymer. To provide evidence for multiblock copolymer formation, the chemical bonds between the SMI and the PTHF blocks were snipped by hydrolysis, leading to its constitutional parts (SMI blocks and PTHF blocks). Hereto, 1 g of the multiblock copolymer was dissolved into 3 mL of DMF, and 1 mL of water and 1 mL of trimethylamine were added. The mixture was heated to 90 °C for 2 days and subsequently for another day. The reaction product was precipitated into a large excess of methanol (a nonsolvent for the remaining SMI blocks and a solvent for the PTHF blocks), filtered, and dried at room temperature.

Instruments. The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) as well as the molecular weight distributions were determined using a Waters 2690 Alliance gel permeation chromatograph equipped with two Styragel HR 5E columns, a Waters 410 differential refractometer, and a Viscotek T50A differential viscometer. The eluent used was THF:acetic acid (95:5 v/v). Absolute molecular weights were calculated by performing universal calibration using polystyrene standards.

Gradient polymer elution chromatography (GPEC) analyses were performed using an Alliance Waters 2690 separation module, equipped with a NovaPak CN modified silica column (150 × 3.9 mm, Waters) set at 35 °C. Solutions of 5 mg/mL of the purified polymer samples in THF were prepared, of which 10 μL was injected. A gradient was applied from 100:0:0, v/v/v heptane:THF + 5% v/v acetic acid:MeOH to 70:30:0 in 5 min

Scheme 1. General Scheme for the Synthesis of a Segmented (SMI-*block*-PTHF)$_n$ Block Copolymer, Using a Polymeric Iniferter Based on an α,ω-Dihydroxy-Terminated Poly(tetrahydrofuran)



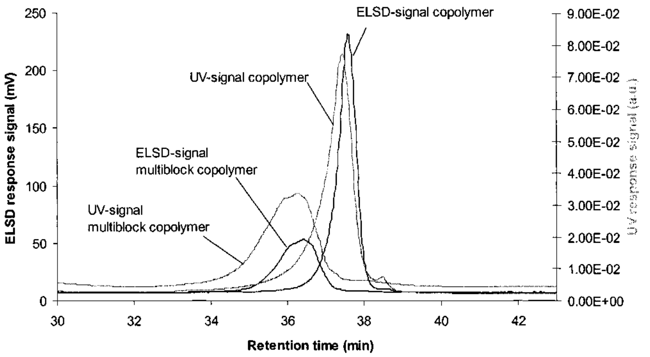


Figure 2. GPEC analysis, using a gradient of heptane to acidic THF, of a styrene-*N*-phenyl maleimide copolymer and a (SMI(*N*-phenyl)-*block*-PTHF)$_n$ multiblock copolymer, containing 12 wt % PTHF-1000 (entry 2 in Table 2).

and then to 0:100:0 from 5 to 40 min. The system was reset stepwise to the initial conditions by pumping through two column volumes of methanol, acidic THF, and then dichloromethane, after which the column was reequilibrated in 30 min with heptane. Detection was done using a PL-EMD 960 evaporative light scattering detector (ELSD, Polymer Laboratories) and with a 2487 Waters dual UV detector at a wavelength of 254 nm. Data were acquired by Millennium 32 3.05 software.

NMR spectra were obtained on approximately 10% w/v solutions in chloroform-d_1 ($CDCl_3$). The spectra were recorded on a Bruker AC-250 spectrometer.

TGA analyses were performed under nitrogen atmosphere on a Perkin-Elmer TGA7 thermogravimetric analyzer at a scanning rate of 10 °C/min.

IR analyses were recorded with a Perkin-Elmer FTIR spectrometer 1720X.

TGA with IR detection was possible by using a TG-IR interface 1700X, Auxiliary Bench 1700X and SYSTEM 2000 TG-IR.

Glass transition temperatures were determined in a second heating with modulated temperature DSC using a TA Instruments 2920 MDSC with a LNCA cooling accessory. A heating rate of 1 or 5 °C/min was used in combination with a modulation amplitude of 1 °C and a modulation period of 60 s. Dynamic mechanical analyses were carried out using a Rheometrics RMS 800 mechanical spectrometer equipped with 25 mm diameter parallel plates.

Results and Discussion

Synthesis and Molecular Characterization of (SMI-*block-PTHF*)$_n$ Block Copolymers. The synthetic route for the (SMI-*block*-PTHF)$_n$ multiblock copolymer based on either *N*-methylmaleimide or *N*-phenylmaleimide, starting from a hydroxy-terminated PTHF, is depicted in Scheme 1. In this study the polymeric iniferter was synthesized from hydroxy-terminated PTHF ($\overline{M}_{\mathrm{n}} = 1000$ g/mol), which was first transformed into chloro-terminated PTHF using thionyl chloride. Subsequently, these chlorine groups were reacted with piperazine, providing secondary amine end groups. Finally, the secondary amine-terminated PTHF was transformed into polymeric thiuram disulfides by reaction with CS_2 and iodine, resulting in a chain-extended PTHF. The synthesized polymeric iniferters were characterized by elemental analysis, SEC/DV, and ^{1}H NMR. SEC/DV showed no traces of nonreacted PTHF. The molecular analysis of the polymeric iniferter has been published elsewhere.[14]

The copolymerization of styrene and *N*-substituted maleimides, thermally initiated by the polymeric PTHF-1000-based iniferter, occurs via an insertion mechanism between the disulfide bonds in the prepared PTHF iniferter. By using the same NMR technique as applied earlier,[14] we were able to determine that the incorporated ratio of styrene and *N*-substituted maleimide (either *N*-methyl or *N*-phenyl) in the SMI blocks was 50/50 mol % and that the incorporated styrene and maleimide units had a predominantly alternating character.

GPEC Analysis of the SMI−PTHF Multiblock Copolymers and a SMI Copolymer. In Figure 2, the elution behavior of a flexibilized SMI(*N*-phenylmaleimide)−PTHF block copolymer containing 12 wt % PTHF-1000 (entry 2 in Table 2) and a SMI(*N*-phenylmaleimide) reference polymer ($\overline{M}_{\mathrm{n}} = 146\,000$ g/mol; $\overline{M}_{\mathrm{w}} = 365\,000$ g/mol) is shown. The difference in elution volume can only be explained by a difference in chemical composition (incorporation of PTHF or not), since the polymers have a similar molecular weight and an identical incorporated ratio of styrene and maleimide. PTHF elutes at a heptane/acidic THF mixture of approximately 60/40 v/v (not shown), while the SMI reference copolymer elutes at about 95% acidic THF (due to interaction with the column material). The broad signal of the multiblock copolymer is probably due to the fact that there are many composition distributions within the molecular weight distribution (e.g., polymers containing a different number of PTHF blocks), which is also visualized in the broad transition of the T_g in Figure 5 (see further).

Snipping of the SMI−PTHF Multiblock Copolymer. To obtain information on the molecular weight distribution of the SMI blocks in the SMI−PTHF multiblock copolymer and in order to collect additional evidence for the existence of SMI−PTHF multiblock copolymers, a SMI(*N*-phenyl maleimide)(50/50)−PTHF-(1000) multiblock copolymer containing 12 wt % PTHF (entry 2 in Table 2) was subjected to a hydrolysis experiment under basic conditions (see the Experimental Section), leading to α,ω-mercapto-terminated SMI copolymers. The chemistry of the degradation reaction is depicted in Scheme 2.

The molecular weight of the multiblock copolymer significantly decreased upon hydrolysis for 2 days ($\overline{M}_{\mathrm{n}}$ from 152 000 to 10 500 g/mol and $\overline{M}_{\mathrm{w}}$ from 363 800 to 19 200 g/mol), and no further decrease was observed by extending the hydrolysis with another day, indicating complete hydrolysis of the thiocarbamate groups. ^{1}H NMR analysis revealed that the hydrolysis product of the hydrolyzed multiblock copolymer did not contain any traces of PTHF, which could be expected, since a

Table 2. PTHF Content, Molecular Weight, $\bar{\nu}_e$,[a] and T_g of Synthesized (SMI-*block*-PTHF)$_n$ Multiblock Copolymers Prepared from PTHF-Based Iniferters

entry of Table 1	SMI block type	PTHF[b] (% w/w)	$\bar{M}_n$ (SEC) (g/mol)	$\bar{M}_w$ (SEC) (g/mol)	$\bar{\nu}_e$ (mol/m^3)	$\bar{\nu}_e$ increase[c] (%)	T_g[d] (°C)
1	styrene-*N*-methylmaleimide	4	95 400	220 600	28 ± 6	27	186 (182)
2	styrene-*N*-phenylmaleimide	12	152 000	363 800	35 ± 6	59	144 (146)
ref[e]	polystyrene	0	500 000	750 000	52	0	100

[a] Calculated with eq 3 from the WG-corrected plateau moduli at 240 °C. [b] Calculated from ^{1}H NMR measurements. [c] Compared to $\bar{\nu}_e$ of unflexibilized SMI copolymers of the same SMI type (=22 ± 5 mol/m^3). [d] T_g values not in parentheses were determined from the second heating curve of a MDSC analysis. T_g values in parentheses were calculated using the Fox relation. [e] Data provided by J. Palmen (DSM Research).

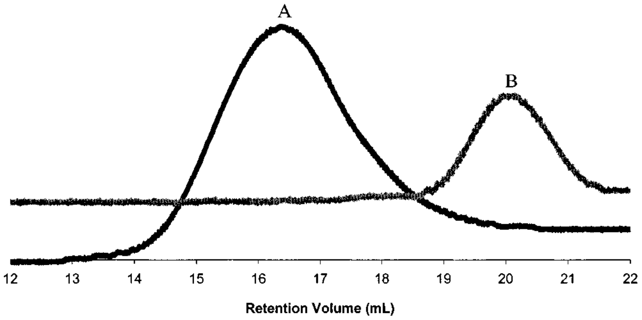
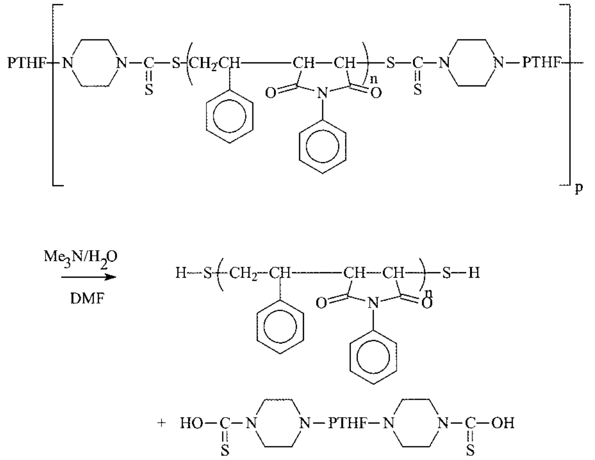


Figure 3. SEC/DV traces of a SMI(*N*-phenyl maleimide)–PTHF multiblock copolymer containing 12 wt % PTHF (A) and the resulting SMI blocks (B) after hydrolysis of the multiblock copolymer (A).

Scheme 2. Degradation Reaction Leading to the Snipping of the Multiblock Copolymer into the SMI Blocks and the PTHF Segments



solution of the hydrolysis product had been added drop by drop to a large excess of methanol, in which the SMI blocks precipitate and the PTHF blocks dissolve. So, the $\bar{M}_n$ of 10 500 g/mol, deduced from Figure 3, is the molar mass of the SMI blocks of the former multiblock copolymer. We also subjected a SMI copolymer (without PTHF blocks) and a PTHF block to exactly the same basic hydrolysis procedure, and in these cases no change in molecular weight was observed, indicating that the only chemistry taking place is cleavage of the main chain C–S bond between the PTHF and the SMI blocks.

The results obtained unambiguously imply that the original SMI- and PTHF-containing copolymer must have been a multiblock copolymer, consisting of several SMI blocks, with an $\bar{M}_n$ of 10 500 g/mol, and of several PTHF blocks, with an $\bar{M}_n$ of 1000 g/mol.

Thermal Stability of the Multiblock Copolymers and the Polymeric Iniferter. In a previous paper[14] it was reported that the segmented (SMI-*block*-PTHF)$_n$ multiblock copolymers exhibit an excellent thermal stability. Apparently, the applied iniferter groups resulted in a structure stable enough to avoid degradation up to at least 300 °C. This is consistent with a previous paper by Clouet et al.,[16] who found that the thermal degradation of dithiocarbamate end groups only starts at temperatures at which the vinyl polymers degrade themselves.

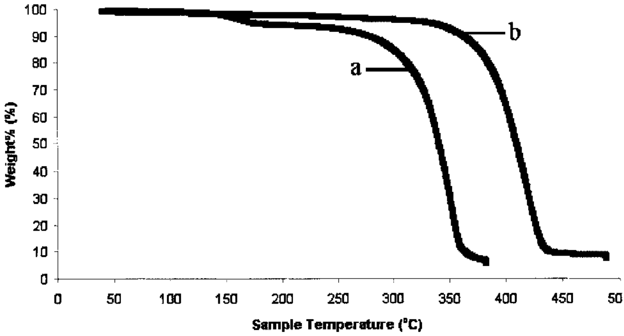


Figure 4. TGA scan of a polymeric iniferter (a) and a (SMI-(*N*-phenyl maleimide)-*block*-PTHF)$_n$ multiblock copolymer (b) containing 12 wt % PTHF-1000 (entry 2 in Table 2) synthesized from this iniferter. The experiments a and b were carried out under N_2 atmosphere and at a scanning rate of 10 °C/min.

Even after a long time in the melt, the molecular weight of the prepared multiblock copolymers remained the same (e.g., for entry 1 in Table 2: $\bar{M}_n$ as synthesized = 95 400 g/mol, $\bar{M}_n$ after 180 min at 200 °C = 95 400 g/mol).

This is an important issue, because the prepared polymers should be stable at the temperatures at which the MDSC and DMA data are acquired. The TGA scan of the segmented copolymer is shown in Figure 4. The polymeric iniferter was subjected to a TGA analysis as well.

As can be seen in the TGA scan of Figure 4, performed under inert conditions, there is a first weight loss of the polymeric iniferter of ca. 6–13 wt % starting around 140 °C. This volatile degradation product was characterized as being CS_2 by gas-phase IR spectroscopy. The degradation path will probably be similar to the decomposition path suggested by Turner et al.,[17] who observed the formation of carbon disulfide during the polymerization of MMA initiated with tetraethyl thiuram disulfide. This degradation reaction implies the scission of the carbon–nitrogen bond, followed by the formation of CS_2.

The temperature at which almost total degradation of the PTHF-based iniferter has occurred is almost 100 °C lower than the temperature at which almost complete degradation of the (SMI(*N*-methylmaleimide)-*block*-PTHF)$_n$ multiblock copolymer has taken place.

Determination of the Glass Transition Temperature of the Synthesized SMI–PTHF Multiblock Copolymers. As can be seen in the MDSC scan of a

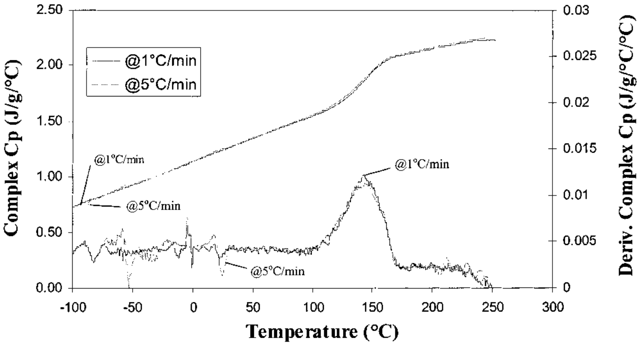


Figure 5. MDSC thermogram of a flexibilized SMI(*N*-phenyl maleimide)−PTHF multiblock copolymer containing 12 wt % PTHF-1000 (entry 2 in Table 2) at two different scanning rates. The two upper curves are the complex C_p signals, whereas the two lower curves are the derivatives of the complex C_p signals.

SMI(*N*-phenylmaleimide)−PTHF multiblock copolymer containing 12 wt % PTHF (see Figure 5), there is no indication for phase separation of the SMI and the PTHF blocks, since only one T_g is detected in the temperature region from −100 to 250 °C (which covers the T_g values of both homopolymers PTHF and SMI). Neither the heat capacity signal nor its derivative dC_p/dT shows an indication of a second low-temperature transition, even though two different scanning rates have been applied to try to distinguish the real transitions. The T_g of the SMI−PTHF multiblock copolymer is situated between the T_g of the pure PTHF blocks (=−74 °C) and the T_g of the SMI(*N*-phenylmaleimide) segments (=221 °C, being the T_g of high molecular weight SMI). The value of this glass transition temperature is about 144 °C, which is in good agreement with the value of 146 °C, calculated with the Fox relation ($1/T_g$ multiblock copolymer = weight % PTHF/T_g PTHF + weight % SMI/T_g SMI). Both prepared multiblock copolymers listed in Table 2 have relatively high T_g values, corresponding to the values calculated with the Fox relation. Moreover, our SMI−PTHF multiblock copolymers are fully transparent, which is to be expected for an amorphous, single-phase material. It should be noted that, thanks to the higher maleimide content of the SMI blocks in the multiblock copolymers compared to those described in ref 12, the miscibility of the SMI blocks with the PTHF blocks has been improved.

The incorporated wt % PTHF is higher than the weighed-in amount of PTHF (cf. Table 1 with Table 2). This can be explained by the fact that the radical polymerization reactions did not reach 100% monomer conversion.

It is also very clear that the molecular weights largely exceed the estimated $\bar{M}_e$ (20 000−30 000 g/mol), implying that reliable rheological experiments can be performed.

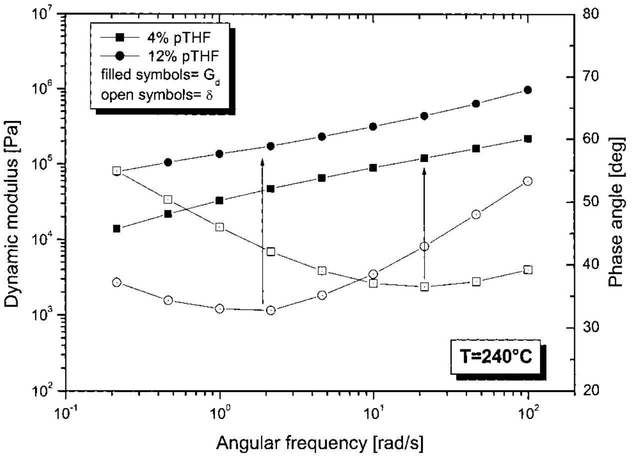


Figure 6. Experimental frequency dependence at 240 °C of complex (or dynamic) modulus (G^* or G_d, filled symbols) and phase angle (δ, open symbols) of the SMI−PTHF multiblock copolymers containing 4 wt % (■ and □, entry 1 in Table 2) and 12 wt % PTHF (● and ○, entry 2 in Table 2).

Determination of the Entanglement Density. The multiblock copolymers containing 4 and 12 wt % of PTHF, for which the discussed molecular and thermal data are shown in Table 2 (entries 1 and 2), were subjected to dynamic mechanical analysis in order to determine the entanglement density. Applying the classical concept of the rubber elasticity theory, the average molecular weight between adjacent cross-links (in the case of rubbers) is inversely proportional to the rubber plateau modulus, G_N^o. This relation has successfully been adapted to determine the average molecular weight between two adjacent entanglements in thermoplastic polymers:[2]

$$\bar{M}_e = \frac{\rho R T}{G_N{}^o} \tag{1}$$

Since the rubbery plateau can hardly be distinguished for most thermoplastic polymers with finite molecular weights, the modulus was taken at the frequency of minimum damping:[18,19]

$$G_N{}^o = [G'(\omega)]tg_{\delta \rightarrow \min} \tag{2}$$

The average entanglement density $\bar{\nu}_e$ can be calculated from the determined plateau modulus:[20]

$$\bar{\nu}_e = \frac{\rho}{\bar{M}_e} = \frac{G_N{}^o}{RT} \tag{3}$$

Although the substituents on the maleimide nitrogen-atom differ for the SMI blocks of the SMI−PTHF multiblock copolymers discussed in this paper, it was shown in a recent paper on a series of nonflexibilized SMIs (containing no PTHF segments) that for relatively small substituents on the maleimide nitrogen, viz. methyl and phenyl groups, the G_N^o is, within experimental error, the same. Only for very bulky substituents on the maleimide nitrogen atom the does G_N^o perceptibly change.[8] This observation allows a direct comparison of the rubber plateau values of the multiblock copolymers listed in Table 2, although the SMI blocks in the case of entry 1 contain 50 mol % *N*-methylmaleimide, whereas entry 2 contains 50 mol % *N*-phenylmaleimide in its SMI blocks. For the SMI−PTHF multiblock copolymers containing 4 wt % PTHF and 12 wt % PTHF (entries 1 and 2 of Table 2, respectively), the experimental frequency dependence of the dynamic or complex modulus (G_d or G^*) and the phase angle (δ) is given in Figure 6.

For the SMI−PTHF multiblock copolymer with 12 wt % PTHF, the experimental rubber plateau modulus at 240 °C was estimated to be 130 ± 15 kPa at a minimum value for the phase angle of 32.8°. For the SMI−PTHF multiblock copolymer containing 4 wt % of PTHF, the experimental rubber plateau modulus at 240 °C was

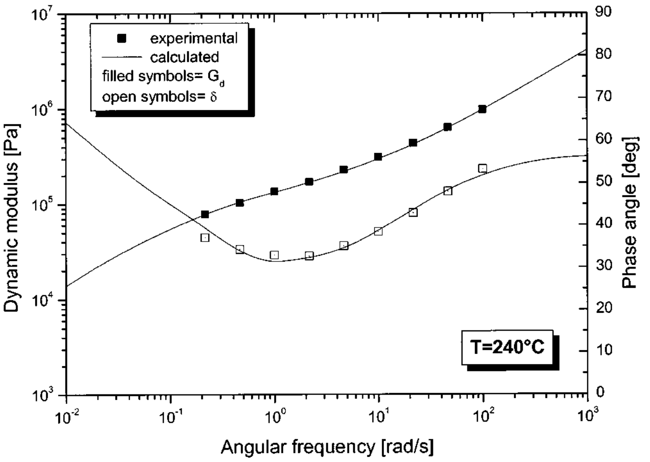


Figure 7. Frequency dependence at 240 °C of complex (or dynamic) modulus (G^* or G_d) and phase angle (δ) of a flexibilized SMI(*N*-phenyl maleimide)−PTHF multiblock copolymer containing 12 wt % PTHF-1000 (entry 2 in Table 2). The symbols correspond to the experimental data (the filled squares match with the modulus, the open squares correspond to the phase angle), whereas the lines represent the model prediction.

estimated to be 96 ± 15 kPa at a minimum phase angle of 36.5°. This plateau modulus proved to be independent of the measuring temperature in the range 230−260 °C. Temperatures exceeding 260 °C proved to cause oxidation of the block copolymers during the long DMA measurements, for which complete oxygen exclusion is impossible. A measuring temperature of 240 °C, however, proved to give us reliable values for $G_N{}^o$, which was the parameter in which we were interested in view of the goal of our research. It is obvious that the multiblock copolymer with the highest wt % of PTHF (and therefore the highest flexibility) exhibits a higher experimental plateau modulus.

However, the high experimental values of the phase angles 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 gives rise to higher modulus values; and

(2) unentangled/relaxing polymeric chains dilute the entanglement network and therefore give 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. To get a more quantitative indication of the plateau modulus, the model of Wasserman and Graessley (WG)[21] was used to predict the linear viscoelastic properties of the flexibilized SMI melts from their absolute molar mass distributions, as determined with SEC/DV. The dynamic properties were calculated assuming a BSW type relaxation time spectrum 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.

Figure 7 illustrates a typical example of model calculations for the flexibilized SMI(*N*-phenylmaleimide) copolymer, containing 12 wt % PTHF-1000 (entry 2 of Table 2). The solid lines are the results of the calculations with the Wasserman−Graessley model, with optimized relaxation parameters, being M_e = 31 200 g/mol, M_c = 62 400 g/mol, G_N = 150 kPa, τ_k= 4 × 10^{-12} Pa s, a = 3.38, t^* = 35 × 10^{-3} s, and β = 0.67 for the SMI(*N*-phenyl maleimide) containing 12 wt % PTHF-1000. 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 $G_N{}^o$, only a limited range of values could be used. For the SMI(*N*-phenyl maleimide) containing 12 wt % PTHF-1000, we found a Wasserman−Graessley (WG)-corrected value of 150 ± 25 kPa (at 240 °C), corresponding to a $\bar{\nu}_e$ of 35 ± 6 mol/m^3, which was calculated with expression 3. For the SMI(*N*-methylmaleimide) containing 4 wt % PTHF, we found a WG-corrected value of 120 ± 25 kPa (at 240 °C), corresponding to a $\bar{\nu}_e$ of 28 ± 6 mol/m^3.

Compared to the WG-corrected values of $\bar{\nu}_e$ of the unflexibilized SMI reference polymers, being 22 ± 5 mol/m^3 for SMI(*N*-methylmaleimide) and 22 ± 5 mol/m^3 for SMI(*N*-phenylmaleimide),[8] there is an increase of respectively 59% for the *N*-phenyl maleimide-based polymer containing 12 wt % PTHF-1000 and only 27% for the *N*-methyl maleimide polymer containing 4 wt % PTHF-1000.

A rise of ca. 60% in entanglement density is more significant than the experimental error, which is indicated in Table 2.

Overall, our results on the enhancement of the entanglement density of brittle SMI copolymers are promising, since the desired high T_g values are also reached. Whether the enhanced $\bar{\nu}_e$, as expected, results in an increased toughness must be verified soon.

Conclusions

It is clear that the polymeric iniferter technique is an excellent technique to synthesize single-phase multiblock copolymers of styrene-*N*-substituted maleimide copolymers and poly(tetrahydrofuran) blocks under thermal polymerization conditions. These multiblock copolymers show excellent thermal stability, which is necessary for industrial processing and for bulk characterization in the melt.

The entanglement densities of these multiblock copolymers exhibit an increase of more than 50% compared to the nonflexibilized SMI polymers. Since entanglement density is thought to be directly related to toughness, this implies that our concept of toughening intrinsically brittle (rigid) polymers, seems to work.

The glass transition temperatures of the flexibilized SMI multiblock copolymers are in the range of 130−150 °C, allowing applications up to 120−140 °C, which is higher than for polystyrene (PS) with a T_g of ca. 100 °C. On the other hand, the incorporation of 12 wt % flexible links into the SMI main chain still does not raise the entanglement density to the level of the (brittle) PS.

It is obvious that the toughening concept of coupling rigid segments to miscible flexible segments is not limited to styrene-*N*-substituted maleimides and PTHF. A wide variety of amorphous materials with a relatively high entanglement density, a relatively high toughness, and a relatively high T_g could be synthesized by applying the described concept.

Acknowledgment. We are indebted to Prof. M. Biesemans of the High Resolution NMR Center (VUB) for the NMR measurements. We gratefully acknowledge the contributions of J. Palmen and T. Sleijpen (both of DSM Research) for the DMA analysis. We also thank Prof. B. Van Mele of the Department of Physical Chemistry and Polymer Science (VUB) and his staff for their help with the thermal characterizations. DSM Research is acknowledged for the financial support of this project.

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MA020084R