Design of a Series of Preceramic *B*-Tri(methylamino)borazine-Based Polymers as Fiber Precursors: Shear Rheology Investigations

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Received October 5, 2006; Revised Manuscript Received November 30, 2006

ABSTRACT: Oscillatory shear flow of poly[*B*-(methylamino)borazine] was studied for suitability as a melt-spinnable material. Shear rheology experiments show that viscosity of molten poly[*B*-(methylamino)borazine] is temperature dependent following an Arrhenius-type equation. The high value of the flow activation energy is caused by the presence of branched chains and cross-linked portions in the polymer network which supply an intrinsic rigidity to the molecular architecture. Dynamic rheological properties of polymers were measured at their spinning temperatures as a function of the oscillatory frequency. The frequency dependence of the storage and loss moduli as well as the damping factor shows that an appropriate ratio of viscosity to elasticity, i.e., $1 < \tan \delta < 2.3$, is necessary to allow for extrusion while a specific range of elasticity, i.e., $10^4 < G'$ [Pa] $< 3 \times 10^4$, is required for drawing the emerging molten fibers as they solidify into fine-diameter solid filaments without loss of cohesion.

1. Introduction

The preparation of polymer-derived ceramic parts with reliable, improved, or new properties requires the control of the shaping and pyrolysis processes with the understanding of the basic phenomena that take place during such processes. By tailoring the chemistry of preceramic polymers, it is possible to obtain tractable compounds with a wide range of viscoelastic properties that render them potential candidates for shaping processes such as melt-spinning,[1] spin-coating,[2] or infiltration.[3] These shaping processes may be compared to flow and elongation deformations of polymers in which a comprehensive investigation of the rheology is vital to improve their processability and the properties of the final shaped ceramic products.

In our group, we use the melt-spinning process (see the preceding paper[4]) and pyrolysis procedures to prepare polymer-derived boron nitride fibers. Melt-spinning represents a combination of an extrusion process to form the fiber from the polymer melt and an optional on-line fiber drawing that stabilizes the fiber line, reduces the fiber diameter, and aligns the polymeric chains along the fiber axis.[4]

In a general way, it is admitted that two categories of rheological problems cause undesirable instabilities during polymer melt extrusion: (i) wall depletion phenomena inside the spinneret and (ii) thickening of extensional viscosity along the spinning line.[5−7] In addition, using a wind-up unit, the drawing of the molten filament emerging from the spinneret results in a rapid transition from fluid (at the exit of capillary) to solid along the spinning line involving drastic increase in surface-to-volume ratios, i.e., surface tension, thereby causing fiber stresses. Thus, fiber formation by melt-spinning is a free surface deformation process and can be assumed to be a pure uniaxial extension between the spinneret and the wind-up unit. As a consequence, both shear and extension rheology should be considered for studies of the melt-spinning process. However, extensional rheology is complex and difficult to investigate, and current devices do not allow investigation of viscoelastic phenomena at the high values of strain reached upon spinning processes although spinning apparatus can be used to characterize polymers in extensional motion.[7] Furthermore, the deformation steady state required for the measurement is hardly reached during experiments run on extensional rheometers. Results obtained from simple elongation tests are therefore not of great benefit in the case of fiber extrusion, and it is common to use the more conventional shear rheology to characterize the melt-spinnability of polymers through the frequency dependence of polymer melts.[8] Such a technique can simulate all deformations going from small to steady-state one.

Some viscoelastic properties are required to successfully spin preceramic polymers. A typical melt-spinnable preceramic polymer should exhibit non-Newtonian behavior during extrusion. In addition, it should flow readily from the spinneret without necking, i.e., deformation instabilities starting from local reduction in the cross section of the emerging green filament.[9] Last, the viscosity must be sufficiently high at zero shear to allow take-up of the fiber at high drawing velocity without loss of fiber cohesion.

In the preceding paper,[4] we established that poly[*B*-(methylamino)borazines] are successfully spun from the molten state depending on both degree of cross-linking and the ratio between flexible bridging units and rigid inter-ring B−N bonds which compose the polymer network. In this second paper, we investigate the shear flow properties of these poly[*B*-(methylamino)borazines] in their molten state. We provide a detailed picture of the influence of the poly[*B*-(methylamino)borazine] architecture on the rheological behavior, study the role played by rheology in melt-spinning, and predict fundamentally

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10.1021/ma062304x CCC: \$37.00 © 2007 American Chemical Society
Published on Web 01/18/2007

Table 1. Properties and Characteristics of Poly[*B*-(methylamino)borazine][4]

polymer	$T_{\text{thermolysis}}$ [°C]	empirical formulas[a]	T_g [°C]	T_l [°C]	T_{spinning} [°C]	$\%_{NB_3}$ sites (±2)
2	150	$B_{3.0}N_{4.5}C_{2.4}H_{10.1}$	46	150	138	3.4
3	160	$B_{3.0}N_{4.5}C_{2.1}H_{9.6}$	64	160	155	4.5
4	175	$B_{3.0}N_{4.4}C_{2.0}H_{9.3}$	70	175	165	6.5
5	185	$B_{3.0}N_{4.3}C_{1.9}H_{9.1}$	83	185	175	6.8
6	200	$B_{3.0}N_{4.2}C_{1.9}H_{8.7}$	100	200	195	6.8

[a] Empirical formula per monomer unit and normalized to three B atoms.

important issues regarding melt-spinning behavior of such polymers. The valuable viscosity obtained therefrom are useful in adjusting the synthesis conditions, and the knowledge of the various rheological parameters serves in the improvement of the melt-spinning of poly[*B*-(methylamino)borazine]. To our knowledge, such an investigation is being used for the first time to give spinnability assumptions of preceramic polymers.

2. Experimental Section

Polymers were handled inside an argon-filled glovebox. Rheological measurements were carried out at the National Center for Engineering Systems with Complex Fluids (T.U.Timisoara, Romania) by means of a Paar Physica MCR 300 oscillatory rheometer. The geometry selected for these experiments was a plate−plate geometry (nominal gap: 0.5 mm; diameter: 25 mm), and 0.5 g of samples was placed between preheated fixtures plates located in argon and then heated to the spinning temperature (T_{spinning}). Dynamic measurements were carried out in the linear viscoelastic (LVE) region obtained by strain sweep tests, using controlled strain amplitude ($\gamma_0 = 10\%$). From the dynamic shear measurements, the storage modulus G', the loss modulus G'', and complex viscosity η^* are obtained. Polymer properties and characteristics are described in our preceding paper.[4] Table 1 summarizes some of these properties and characteristics which are required for the rheological investigations.

3. Results and Discussion

3.1. Preliminary Studies. Poly[*B*-(methylamino)borazine] samples are characterized by means of shear rheology. An important first step in performing dynamic rheological characterization concerns the determination of the linear viscoelastic (LVE) region in which the dynamic rheological parameters of these polymers have to be independent of the applied strains. In this controlled-strain test, samples are heated at their T_{spinning} and then deformed in oscillatory shear flow up to a maximum strain γ_0 which must be small enough to be in the linear regime but well above the background noise. Then, the time-dependent shear stress $\sigma(t)$ that arises because of sample deformation is monitored. Frequency-sweep tests were carried out on each polymer sample. Figure 1 shows the strain dependence of the storage modulus G', loss modulus G'', and complex viscosity η^* for the representative melt **4** at 165 °C using an oscillatory frequency $\omega = 0.1\ \text{s}^{-1}$.

As observed, **4** displays a constant high plateau value with a critical strain γ_c of about 17%, from which rheological parameters are modified. It is therefore reasonable to propose that $\gamma_0 = 10\%$ represents an appropriate value to maintain constant dynamic moduli with deformation amplitude. Such a value is commonly used in experiments for solids, thermosetting plastics, or polymers.[10] Similar values were obtained for other samples studied here. All plots presented in this work therefore correspond to that selected γ_0.

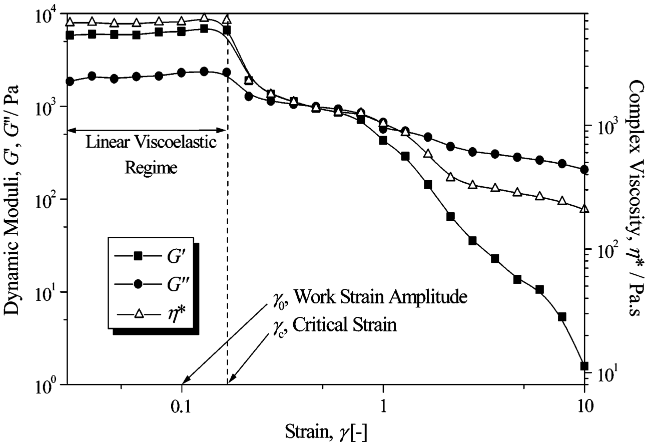

Figure 1. Strain dependence of storage (elastic) modulus, loss (viscous) modulus, and complex viscosity of the representative polymer **4** in its molten state ($T_{\text{test}} = 165$ °C, $\omega = 0.1\ \text{s}^{-1}$).

An important second requirement is that polymers must be thermally stable during the rheological tests to provide reliable rheological data. In our preceding paper,[4] DSC experiments showed that the stability of **2**−**6** as melts extended over a wide range of temperature ($T_l - T_g \sim 100$ °C) and that stable spinning occurred at $T_{\text{spinning}} < T_l$. Such results suggest that polymers will be stable during rheological tests carried out at T_{spinning}. However, it should be mentioned that some polycondensation phenomena known to modify the viscoelastic properties of polymers are poorly exothermic and thus not detectable by DSC experiments. Therefore, the variation of rheological parameters, i.e., G', G'', and η^*, must be checked versus time for each polymer at their T_{spinning}. The good thermal stability of poly[*B*-(methylamino)borazine] as melt was confirmed by such experiments, since values of G', G'', and η^* remain unchanged during 1000 s for melts **3**−**6** (see Figure 1-SI in Supporting Information). In contrast, **2** cannot be considered here because it exhibits a Newtonian flow behavior with negligible elastic components and displays a thermal instability for long-term rheological measurements ($t > 500$ s) at 138 °C most probably due to further cross-linking reactions. Such a rheological behavior can be related to the poor melt-spinnability of this polymer as observed in our preceding paper.[4]

3.2. Temperature Dependence of the Shear Viscosity. At room temperature (RT), poly[*B*-(methylamino)borazines] **3**−**6** are solid and melt upon heating in an inert atmosphere in order to allow melt-spinning. Thus, the shear viscosity should decrease on heating in such atmospheric conditions. Therefore, we propose that the temperature dependence of the shear viscosity follows an Arrhenius-type equation according to eq 1.[11]

$$\ln \eta = \ln A - \frac{E_a}{RT} \tag{1}$$

where A is a constant, R the gas constant, E_a the activation energy, and T the temperature (in Kelvin).

Figure 2 shows the plot of ln η vs $1/T$ of the representative polymer **4** at $\omega = 0.1\ \text{s}^{-1}$ according to eq 1.

It should be mentioned that experiments shown in Figures 1 and 2 were performed at $\omega = 0.1\ \text{s}^{-1}$ in order to have the data as close as possible to "zero shear viscosity". At lower frequencies, possible influence of polycondensation phenomena

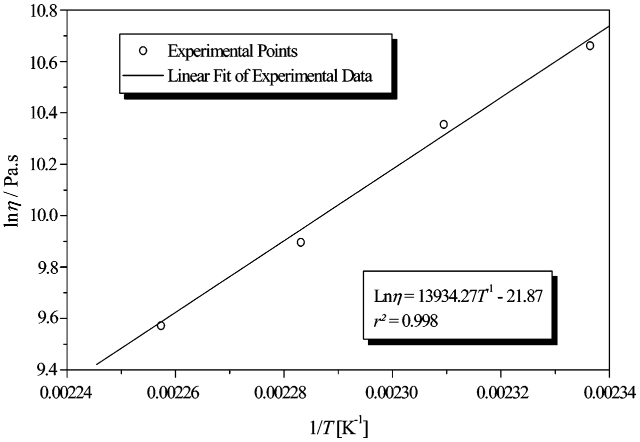

Figure 2. Plot of ln η vs $1/T$ for **4** at $\omega = 0.1\ \mathrm{s}^{-1}$.

might affect the rheological measurements due to the long time of experiments.

Experimental data plots are fitted with relatively good agreement with eq 1. The apparent activation energy for **4** calculated from the slope is ~116 kJ/mol. Since there are no such data available for borazine-based polymers and very little for general preceramic polymers, e.g., poorly melt-spinnable polycarbosilanes[12] display an activation energy of ~180 kJ/mol, comparison was made with common linear polymers whose flow activation energies are generally lower than 70 kJ/mol.[13−19] Such a difference in energy values means that the viscosity of poly[*B*-(methylamino)borazine] is considerably more temperature sensitive than that of linear polymers. This is a primary reason why poly[*B*-(methylamino)borazines] are spun in a narrow and strict temperature range ($T_{\mathrm{spinning}} \pm 1$ °C).[4] Besides, it is remarkable to observe that values of η at a given temperature are relatively high in the molten state and especially higher than those of common linear polymers. Keeping in mind that the melt viscosity is closely dependent on the polymer architecture, such a finding corroborates definitely the fact that the overall structure of a typical melt-spinnable poly[*B*-(methylamino)borazine] is highly branched, causing poor molecular motion. In addition, it is reasonable to speculate that the plasticizing $-\mathrm{N(H)CH_3}$ groups identified in these polymers provide strong intermolecular interaction, causing different frequencies dependence of the viscosity. However, even though our results are in complete agreement with rheological studies performed on preceramic polycarbosilanes,[12] melt rheology of borazine-based polymers has not yet been investigated, and therefore, there is a lack of evidence or discussion in the literature to support our contentment with regards to the melt viscosity of poly[*B*-(methylamino)borazine].

3.3. Frequency Dependence of Rheological Parameters. Measurements of the viscosity and elasticity of molten polymers at their spinning temperature is important for controlling the melt-extrusion process and the subsequent drawing of the derived molten filament. The frequency dependence of the rheological parameters was determined during dynamic frequency sweep experiments within the LVE range, giving the behavior of **3**−**6** vs the oscillatory frequency (Figures 3−5). As-plotted curves showing the frequency dependence of G' (black square), G'' (black circle), and η^* (empty symbols) for the different melts help us to predict the melt-spinnability of poly[*B*-(methylamino)borazine]. Assuming the Cox−Merz relation[18] to be applied, it should be mentioned that we suppose that ω is related to the shear rate within the capillary. Therefore, we propose that the oscillatory frequency is proportional to a certain extent to the extrusion velocity.

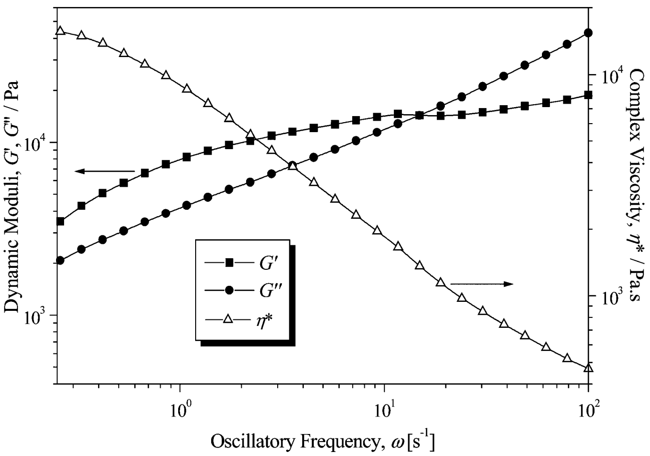

Figure 3. Frequency dependence of G', G'', and η^* for **4** at $T_{\mathrm{test}} = 165$ °C.

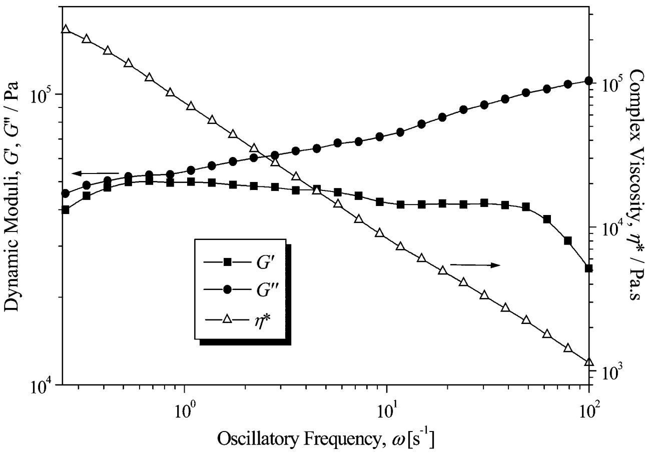

Figure 4. Frequency dependence of G', G'', and η^* for **5** at $T_{\mathrm{test}} = 175$ °C.

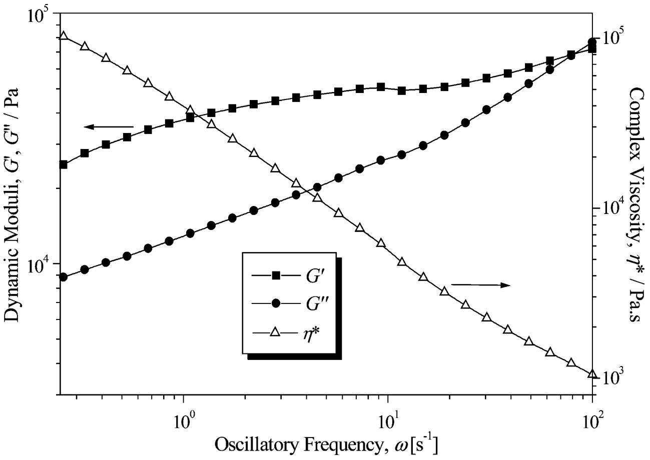

Figure 5. Frequency dependence of G', G'', and η^* for **6** at $T_{\mathrm{test}} = 195$ °C.

It should be noticed that rheological results concerning samples **3** and **4** are similar. Therefore, for simplification, only results concerning the polymer **4** are reported.

As shown in the log−log plots in Figures 3−5, the complex viscosity η^* of **4**−**6** follows the same trend. It is seen to continuously decrease in the oscillatory frequency range 0.25−100 s^{-1}, indicating clearly the shear-thinning behavior of poly[*B*-(methylamino)borazine] melts. Therefore, poly[*B*-(methylamino)borazine] investigated here are non-Newtonian compounds as is usually required for melt-spinnable polymers. Besides, it can be seen that the magnitude of η^* of **4** is lower than those of **5** and **6** at a given ω. Such differences are caused by the occurrence of intramolecular cross-linking and the increase of the relative amount of inter-ring B−N bonds (Table 1) going from **4** to **6** we have identified in our preceding paper.[4]

Regarding storage and loss moduli as a function of test frequency, it can be seen that polymer melts reveal an increase of the magnitude of G'' with increasing oscillatory frequency which is due to the higher energy required for molecular viscous response. The slight increase of the magnitude of G' for melts **4** and **6** is attributed to a decrease in time available for molecular relaxation.

There are three distinct sets of behavior illustrated in the plots in Figures 3−5.

The first applies to **4** ($T_{\mathrm{test}} = 165$ °C; Figure 3). It can be seen that its elastic behavior remains predominant (i.e., G' is larger than G'') in the frequency range 0.25−16 s^{-1}. At $\omega = 16\ \mathrm{s}^{-1}$ occurs the crossover of G' and G'', and the viscous component (G'') becomes larger than the elastic component (G') above that oscillatory frequency. A slight stagnation of G' is observed between $\omega = 16\ \mathrm{s}^{-1}$ and $\omega = 100\ \mathrm{s}^{-1}$, whereas G'' continues to increase in the oscillatory frequency range.

5 ($T_{\mathrm{test}} = 175$ °C; Figure 4) exhibits a relatively different rheological profile. The higher magnitude of G'' compared to that of G' within the whole oscillatory frequency region suggests a predominant viscous behavior in the molten state. No crossovers between G' and G'' are observed in the frequency range investigated here. It is interesting to note that values of G' reach a plateau at $\omega = 0.5\ \mathrm{s}^{-1}$ and remain nearly constant in the range 0.5−40 s^{-1}. The strong decrease of G' above $\omega = 40\ \mathrm{s}^{-1}$ reveals a loss of elasticity most probably due to the collapse of the polymer structure under the high level of shearing applied at such values of ω.

In contrast to **5**, dynamic moduli continuously increase with the oscillatory frequency for **6** ($T_{\mathrm{test}} = 195$ °C; Figure 5). The viscous component of **6** remains lower than the elastic component within the whole oscillatory frequency region, revealing the elastic-dominant response of this polymer during melt-spinning. A crossover point is found at $\omega = 90\ \mathrm{s}^{-1}$.

Such results provide data which are legitimate for the understanding of the melt-spinning bahavior of poly[*B*-(methylamino)borazine]. Fundamental assumptions for melt-spinning are given below.

On the basis of the poor melt-spinnability of **6**,[4] it is reasonable to assume that an excess of G' over G'' is undesirable for reliable melt-spinning. Working on this assumption, we state that melt-spinning of **4** is achieved above the crossover of G' and G'' at $\omega = 16\ \mathrm{s}^{-1}$, at which the viscosity component becomes predominant. This is in excellent agreement with spinning experiments, since this polymer displays excellent extrusion ability as melt at relatively high extrusion velocity.[4] As a first prerequisite condition for melt-extrusion, we therefore assume that the viscous component (G'') must be higher than the elastic one (G') in the frequency range investigated here. On the basis of this requirement, polymer **5** should be successfully extrudable from its molten state into fibers. Spinning experiments are in good agreement with such predictions, but a cohesive fracture occurred at high drawdown ratio ($\kappa > 93.9$).[4] This spinning behavior is probably caused by the loss of elasticity of this polymer under the high shearing level identified in Figure 4. As a first assumption for an appropriate filament drawing, we therefore suggest that a minimum level of elasticity is needed and/or the loss of elasticity must be restricted during rheology tests.

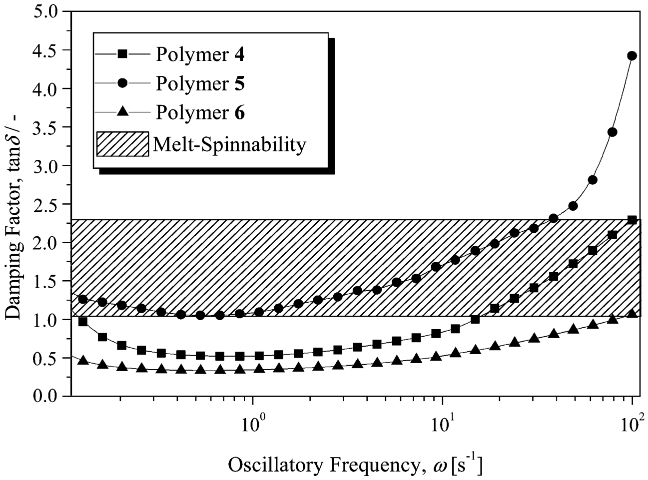

Figure 6. Frequency dependence of tan δ for **4**−**6** at their corresponding T_{spinning}.

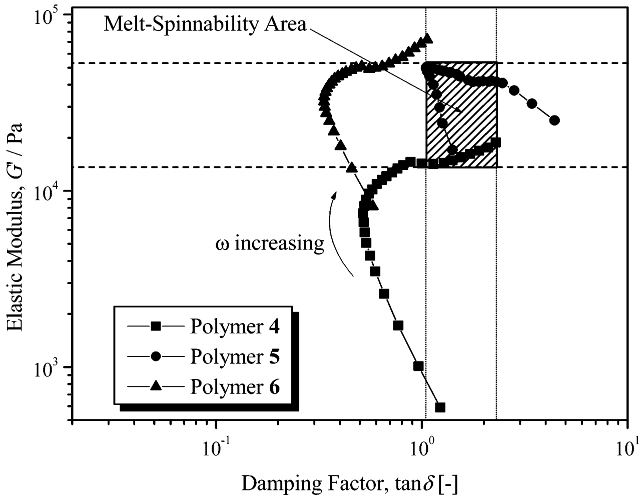

Figure 7. Variation of G' vs tan δ for **4**−**6**.

From a rheological point of view, these established spinnability requirements are consistent with both phenomena occurring upon melt-spinning which have been briefly described in the Introduction. First, the G'' to G' ratio, i.e., damping factor tan δ, is closely correlated to the melt-extrusion process, since the latter requires an appropriate viscosity-to-elasticity ratio, allowing deformation of the molten polymer by flowing through the spinneret and then retention of the filament shape at the capillary exit. Second, the elastic modulus is connected to the stretchability of the emerging molten filament which must exhibit a minimum level of elasticity to ensure cohesion of the material along the spinning line and then retention of the fiber shape as it solidifies.

3.4. Melt-Spinnability Criteria. Figures 6 and 7 offer fundamental data about the rheological behavior of poly[*B*-(methylamino)borazine]. Figure 6 presents the frequency dependence of tan δ.

First, Figure 6 shows that the slope of the tan δ curve is negative in the low-oscillatory frequency range ($\omega \leq 0.6\ \mathrm{s}^{-1}$) and becomes positive above that value up to $\omega = 100\ \mathrm{s}^{-1}$. Second, the study of Figure 6 allows the establishment of a tan δ range in which polymers are considered extrudable as melt. As previously predicted, an excess of the viscous component over the elastic one, i.e., tan $\delta > 1$, seems to be required for spinning poly[*B*-(methylamino)borazine] melts in the oscillatory frequency range investigated here. Referring to the excellent

Table 2. Beyreuther's Spinnability Criteria[20]

tan δ	G' [Pa]	observed spinnability
≤ 5	100	none
5−10	100	medium
≥ 10	100	high

melt-spinnability of **4** ($V_{\text{extrusion}} = 0.042$ m/s and $\kappa = 111.9^4$) and the appreciable spinning behavior of **5** ($V_{\text{extrusion}} = 0.033$ m/s and $\kappa = 93.9^4$), it is also reasonable to fix a maximum value of 2.3 for tan δ in the oscillatory frequency range investigated here.

Following the above-described classification, melt-spinnability criteria can be stated by plotting the values of G' vs tan δ (Figure 7).

The informative graphic presented in Figure 7 shows that a minimum value of elasticity, i.e., 1×10^4 Pa, and a maximum one fixed at 5×10^4 Pa are required for spinning poly[*B*-(methylamino)borazine].

Because there are any such predictions available for preceramic polymers to date, our rheological predictions were compared with those already established for common organic polymers.

Change in melt-spinnability of common polymers as a function of tan δ was studied in few works.[10,19] In these studies, it was shown that melt-spinnable polymers could form wires in extension above a certain ratio of dynamic moduli, but very few details were given concerning the value of tan δ required for production of fibers from these melts. In addition, nothing was provided about elasticity threshold enabling the spinnability phenomenon.

Beyreuther et al.[20] proposed requirements for melt-spinning polyolefin-type polymers based on shear rheology investigations. Results were checked by Hoffmann et al.[21] based on the correlation between the shear rheology in small-angle oscillation, tan δ, and spinnability of polymer. These authors established empirical conditions about spinnability of these polymers and classified them in three categories going from nonspinnable compounds to well-spinnable ones. Based on their classification, an appreciable spinnable polymer displayed tan δ and G' values above 10 and 1×10^2 Pa, respectively. Table 2 summarizes spinnability criteria based on rheology curves for polyolefin-type polymers.

Criteria defined by Beyreuther et al.[20] are well distinct from our predictions established in the present paper. Results reported in Table 2 even predict that poly[*B*-(methylamino)borazines] represent nonspinnable compounds, whereas spinning experiences showed that some of them display reliable spinnability (polymers **3**−**5**).[4] Such contradictions reflect significant differences in the molecular architecture of the respective polymers as already mentioned in our preceding paper. Melt-spinnable polyolefins such as thermoplastic polyethylene ($-(CH_2-CH_2)_n-$) or polypropylene ($-(CH_2-CH-CH_3)_n-$) are soft and pliable organic polymers constituted of linear carbon chains made of several tens of thousands of monomer units free of cross-linked portions. The poor degree of cross-linking and the lack of strong interactions between the chains provide high polymer meltability and therefore a predominant viscous character. Thus, in contrast to poly[*B*-(methylamino)borazine] displaying cross-linked portions of the type $-N(CH_3)-$ bridges and NB_3 sites, these linear organic polymers have an intrinsic high G''/G' ratio.

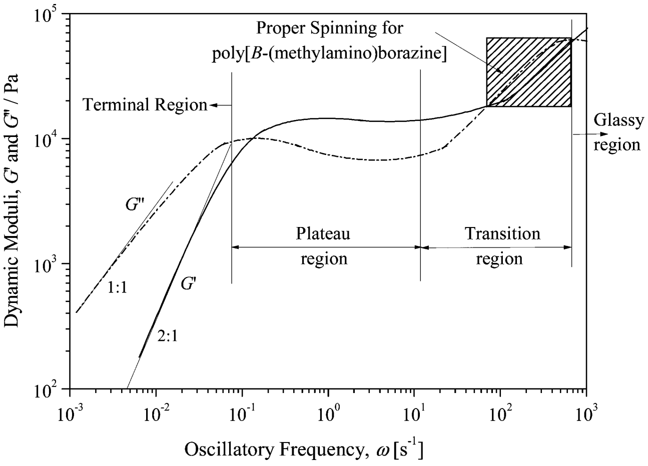

Figure 8. Qualitative G' and G'' curves shape for polymer melts.[22]

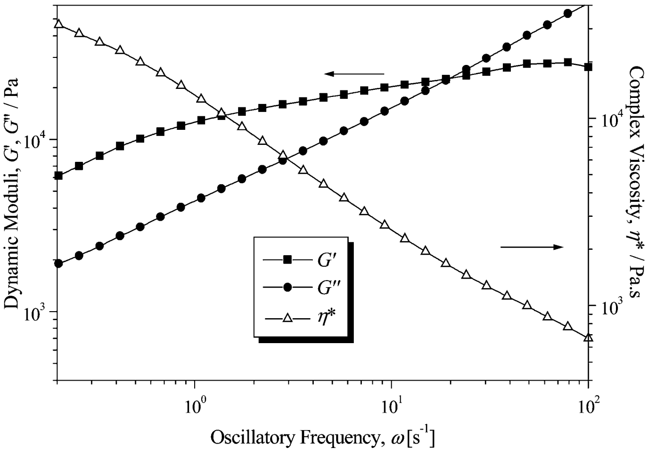

Figure 9. Frequency dependence of G', G'', and η^* for **4** at $T_{\text{test}} = 160$ °C.

The effect of the overall structure of poly[*B*-(methylamino)borazine] on both the rheological profile and melt-spinnability is highlighted by plotting the frequency dependence of viscoelastic moduli G' and G''. The inset represented by Figure 8 shows the frequency dependence of G' and G'' for general polymer melts.[22] Referring to melt-spinnability of poly[*B*-(methylamino)borazine], our melt-spinnability criteria are fulfilled in the transition region in which G'' is larger than G', the latter being higher enough ($G' > 1 \times 10^4$ Pa).

Whereas the plateau region is known to reflect the dominance of long fragments of the polymer chains, i.e., the backbone of linear organic polymers, the transition region corresponds to the effect of the shortest parts of the macromolecules such as chain branching.[22] This observation clearly confirms that rheological behavior and melt-spinnability of poly[*B*-(methylamino)borazine] are rather governed by the cross-link density of the polymer network.

It is relevant to mention here that computing the values of G' and G'' for the three samples cannot be satisfactorily achieved, although the G' and G'' curves of poly[*B*-(methylamino)borazine] fit the general pattern of polymers. The classical mathematical functions which define the relaxation spectrum are unable to properly fit both dynamic moduli with the same values of material functions. More investigations need to be done before we can have a better understanding of this phenomenon.

3.5. Effect of Temperature of Rheological Tests on the Viscoelastic Properties of Polymers. Figures 9 and 10 plot the frequency dependence of η^*, G', and G'' for **4** at 160 (Figure 9) and 170 °C (Figure 10). Tests performed at its ideal T_{spinning} (i.e., 165 °C) were reported in Figure 3 and discussed above. It should be mentioned that the experimental data obtained from

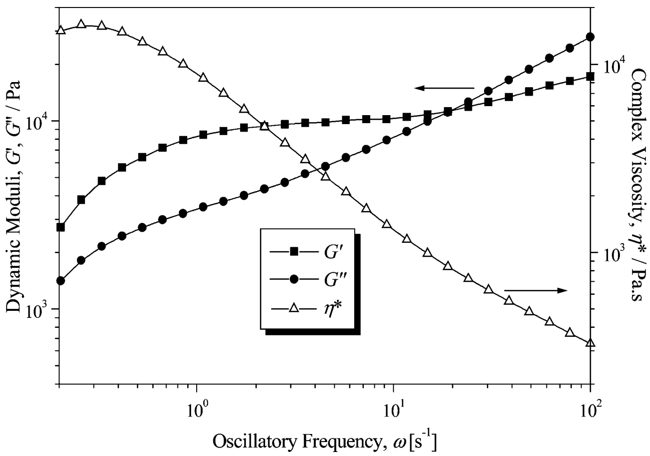

Figure 10. Frequency dependence of G', G'', and η^* for **4** at $T_{\text{test}} =$ 170 °C.

the rheological tests carried out at 175 °C are not reported in those figures, since the polymer was found to be chemically unstable at that temperature for long-term measurements due to the occurrence of enhanced cross-linking.

As already seen at $T_{\text{test}} = 165$ °C (Figure 3), **4** exhibits a shear-thinning behavior in the molten state at 160 and 170 °C, but it is interesting to observe that this non-Newtonian behavior is becoming more pronounced with increasing temperature as illustrated with the decreased slope of the corresponding curve going from −0.65 ($T_{\text{test}} = 160$ °C) to −0.81 ($T_{\text{test}} = 170$ °C). This can be related to the increase of the chain mobility in the polymer upon heating as previously described for the temperature dependence of the viscosity. It should be noted that other polymers show similar behavior.

The behavior of G' and G'' as a function of the oscillatory frequency at 160 and 170 °C is similar to that obtained at 165 °C. Likewise, it is shown that G' and G'' increase with ω for each temperature, and the elastic behavior remains predominant at low and intermediate frequency. At a certain frequency, the crossover of G' and G'' occurs, and the viscous component becomes larger than the elastic component. The position of this crossover point remains at a constant frequency ($\omega \sim 16$ s^{-1}) going from 160 to 170 °C.

By comparing the relative behavior of G' and G'' independently, it is observed that an intermediate-frequency plateau tends to appear at 165 °C (Figure 3) and is formed at 170 °C (Figure 10) in the curve reporting the plot of G' data. This could be considered as a result of the onset of cross-linking reactions, since such temperatures are close to the temperature at which polymerization restarts ($T_1 = 175$ °C[4]) for the related polymer. In contrast, the magnitude of G'' monotically decreases with increasing temperature as illustrated with the decrease of the slope from 0.56 ($T_{\text{test}} = 160$ °C) to 0.48 ($T_{\text{test}} = 170$ °C). In all cases, the values of G' after the crossover point are above the minimum value ($G' > 10^4$) previously predicted for an appreciable drawing of the molten filament.

Figure 11 shows the oscillatory frequency dependence of tan δ. For an appropriate comparison, the data obtained at 165 °C are inserted in Figure 11.

Referring to the previously reported spinnability assumptions for tan δ, it can be postulated on the basis of Figure 11 that the polymer **4** is extrudable at relatively high extrusion velocity in a wide range of temperature going from 160 to 170 °C, since the values of tan δ cover the range 1.0−2.3 at relatively high oscillatory frequency in which melt-spinnability was considered optimal. This is confirmed by plotting G' values as a function of tan δ for temperatures covering the range 160−170 °C (Figure 12).

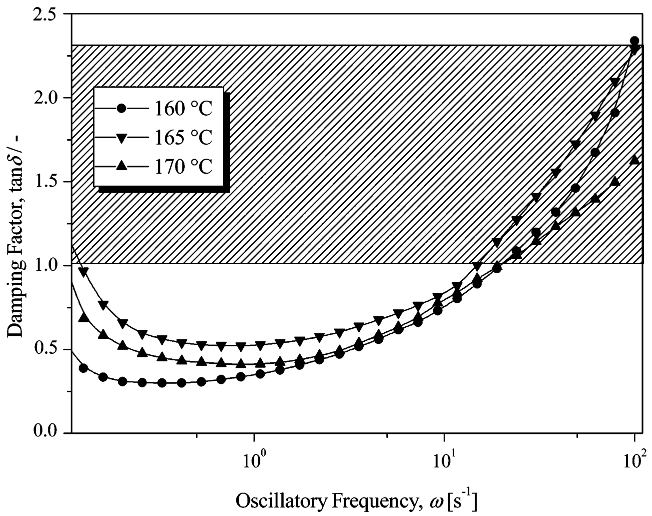

Figure 11. Values of tan δ for **4** in the temperature range 160−170 °C.

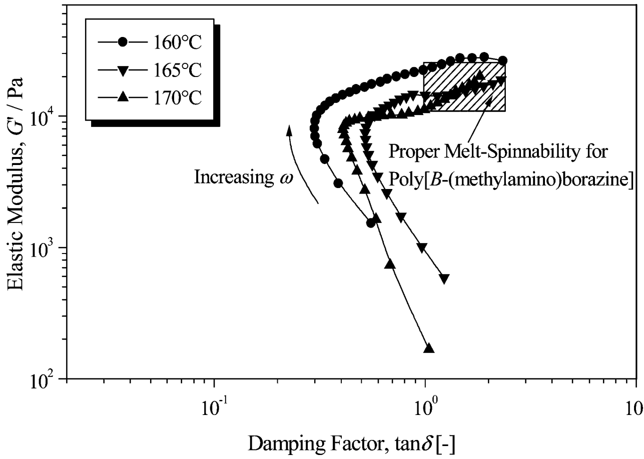

Figure 12. Variation of G' vs tan δ for **4** at different temperatures.

Table 3. Experimental Conditions and Observations during Spinning of 4

T_{spinning} [°C]	$V_{\text{extrusion}}$ [m/s][a]	$V_{\text{take-up}}$ [m/s][b]	κ[c]	exptl fibers diam [μm][d] (±1)	spinnability
160	0.037	2.1	56.8	28	poor
165	0.042	4.7	111.9	17.5	high
170	0.047	4.7	100	20.5	medium
175	0.050				none

[a] Calculated from the piston velocity via volume displacement at a pressure of about 350 N; maximum measured velocity. [b] Maximum measured velocity. [c] Defined as the drawdown ratio, $\kappa = V_{\text{take-up}}/V_{\text{extrusion}}$; see ref 23. [d] Average of 50 readings taken wih the CCD camera and confirmed with a digital micrometer.

In a first approximation, we predict that polymer **4** is melt-spinnable in a range of temperature of 10 °C, since all experimental plots at temperatures going from 160 to 170 °C are in the G' range established above (Figure 12). Such a result is in contradiction with those obtained during the study of the temperature dependence of the viscosity which presumed that spinning of poly[*B*-(methylamino)borazine] should be achieved in a strict and narrow temperature range.

In order to check these spinnability assumptions for poly[*B*-(methylamino)borazine], melt-spinning experiments of **4** were carried out in the temperatures range 160−175 °C. Table 3 reports experimental conditions for melt-spinning.

At 160 °C, melt-extrusion quality was good as illustrated by the intermediate extrusion velocity which is applied to form the filament from the melt (Table 3). Nevertheless, although the as-extruded molten filament exhibits a regular shape, drawing remains poor ($\kappa = 56.8$), since numerous fiber breakages were encountered at low take-up velocity ($V_{\text{take-up}} = 2.1$ m/s). This is caused by a poor meltability of the polymer at such a temperature. As previously studied in our preceding paper,[4] the polymer spinnability was excellent at 165 °C. A drawdown ratio as high as 111.9 is reached without breakage of the extruded filament. At 170 °C, the melt appears more fluid and easily extrudable ($V_{\text{extrusion}} = 0.047$ m/s), but the as-extruded filament line shows some signs of capillary instability. However, the melt-spinnability at that temperature can be considered as suitable, since a maximal drawdown ratio of 100 is applied to the filament. At 175 °C, the polymer flowed through the die as a Newtonian fluid, i.e., easily extrudable but capillary instability in such a way that drawing is not possible. Finally, assumptions made on the basis of values of tan δ appropriately predict the ability of the polymer **4** to be extruded at various temperatures. In contrast, on the basis of melt-spinning experiments, we propose to reduce the G' range previously given and fix an upper limit for the elasticity modulus. Figure 12 shows that the requirements for drawing the **4**-derived filament are equivalent to value of G' in the range $1 \times 10^4 - 3 \times 10^4$ Pa. It should be mentioned that the melt-spinnable polymer **5** is included in this restricted range for G'.

4. Conclusion

Viscoelastic properties of a series of poly[*B*-(methylamino)-borazines] have been investigated in the molten state by means of oscillatory shear flow. The aim of the present study was to correlate the rheological behavior of such preceramic polymers with their molecular structure and provide some spinnability criteria which predict the melt-spinnability of poly[*B*-(methylamino)borazine]. Results indicated that the flow activation energies of poly[*B*-(methylamino)borazines] measured during the measurement of their viscosity as a function of the temperature is high presumably due to the rigid nature of the basal polymeric network. In the present paper, the most suitable conditions for melt-spinning of poly[*B*-(methylamino)borazine] were investigated from the viewpoint of the complex viscosity, storage modulus, and loss modulus. The following conclusions are drawn:

(i) The complex viscosity η^* is seen to decrease with increasing oscillatory frequency ω, indicating clearly the shear-thinning behavior of poly[*B*-(methylamino)borazine] melts during extrusion. This is a well-known prerequisite condition for melt-spinnable polymers.

(ii) It is clearly demonstrated that (i) an appropriate ratio of the viscous (G'') to the elastic (G') portion is necessary to allow fiber formation during extrusion of the polymer and (ii) a minimum level of elasticity is required for drawing the emerging molten filament into a fine-diameter solid filament. As a consequence of the rheological study and the melt-spinnability behavior, the damping factor (tan δ) and elastic modulus (G') have to reach the following conditions:

$$1 < \tan \delta < 2.3$$

$$1 \times 10^4 \text{ Pa} < G' < 3 \times 10^4 \text{ Pa}$$

As a consequence and taking into account the mechanical properties of polymer-derived ceramic fibers are directly connected to the polymer melt-spinnability, it is established that polymers prepared between 160 and 185 °C display appropriate rheological properties to successfully prepare high-performance BN fibers.

Acknowledgment. The authors gratefully acknowledge the support of the members of rheology group from the National Center for Engineering Systems with Complex Fluids, T. U. Timisoara (Romania), director Prof. Romeo Resiga, for their contribution to rheology measurements. We thank the European Community who supported this work through the Marie Curie Research Training Network PolyCerNet (Contract MRTN-CT-2005-019601).

Supporting Information Available: Figure 1-SI showing stability test of **4** at its spinning temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA062304X