Macromolecules **2003,** *36,* 3749−3757

Linear and Nonlinear Rheological Properties of Self-Assembling Tectons in Polypropylene Matrices

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Received July 16, 2002

ABSTRACT: The supramolecular assembling of small, equimolar amounts of octyl-substituted complementary tectons based upon barbituric acid (BA) and 2,4,6-triaminopyrimidine (TP) in an isotactic and, particularly, in an atactic polypropylene matrix was studied by means of dynamic-mechanical spectroscopy. Self-organization of these tectons within the matrix depends on temperature and concentration of tectons and leads to network-like behavior, which is accompanied by drastic changes of the melt rheology of these compounds in comparison to the pure matrix. In addition to external parameters such as temperature, the formation of a tecton network which sets in for a concentration of 2 wt % and higher is determined by the enthalpic interactions between matrix and tectons. It turned out that none of the thermorheological and viscoelastic properties of the compounds depend on tacticity. Strain-sweep experiments reveal the extreme shear sensitivity of the formed supramolecular structures. Moreover, these experiments show that in all samples a certain amount of tecton (approximately 1%) remains dissolved and thus constitutes an “effective matrix” in which the network formation occurs. An estimation of the critical deformation, which is on the order of magnitude of 10^{-4}, was achieved by means of creep experiments.

Introduction

New developments in nanostructured polymeric materials are highly stimulated by recent innovations in supramolecular chemistry and its novel approach to complex molecular and supramolecular architectures. Because of the spontaneous recognition-driven association of small molecules, which have the function of monomers (according to Wuest[1] these monomers represent “tectons“, i.e., “frameworks with sticky sites”), linear, branched, helical, fiberlike, and other superstructures are formed by exploiting physical interactions (mostly the formation of hydrogen bridges) between complementary donor/acceptor-type tectons. Several groups report the use of supramolecular assemblies to produce nanostructured materials in organic and aqueous media as reviewed by Terech and Weiss.[2] Because of their ability to convert the low viscous solvent to a transparent gellike state, these tectons are also called gelators, and the process of superstructure formation is paralleled with gelation.

Supramolecular nanostructure formation is also of great industrial significance if it takes place in melts and plays a key role for example in the nucleation and crystallization of polyolefins. For example, dibenzylidene sorbitol (DBS) and its derivatives are well-known nucleating agents and clarifiers for polypropylenes (PP, see e.g. Shepard et al.,[3] Thierry et al.,[4] and Maier et al.[5]). Shepard and co-workers[3] described the gel formation as three-dimensional self-assembling of DBS molecules, leading to connected nanofibrils within the polypropylene matrix. Similar results for DBS in a poly(ethylene oxide) (PEO) matrix have been reported by Thierry and co-workers.[4] The addition of only parts of 1% of tectons to the matrix changes not only the self-organization of the tectons in comparison to their neat state but even more dramatically the rheological properties of the matrix.

These properties have been investigated intensively by Fahrländer et al.[6] and Mercurio et al.[7] They found several peculiarities of the linear and nonlinear viscoelastic properties of these materials which are associated with very slow power law type relaxation and an extreme shear sensitivity.

Recently, we reported investigations of nanostructure formation achieved by means of supramolecular self-assembly of tectons based upon substituted barbiturates combined with complementary derivatives of 2,4,6-triaminopyrimidines.[8,9] In equimolar mixtures of these molecules each complementary pair forms a tecton by the help of three hydrogen bonds (see Figure 1). The tectons themselves interact with other tectons by hydrogen bonds and therefore self-organize into ribbonlike structures that exhibit a layered morphology. We have examined the self-assembly of octyl-substituded tectons (OT) in the pure state as well as in polymer melts (polystyrene, PS, and poly(methyl methacrylate), PMMA). The morphological analysis of the PS compounds revealed—similar to DBS—fibrilar organization of the tectons.

The corresponding rheological experiments showed that supramolecular self-assembling of substituted barbituric acids (BA) and 2,4,6-triaminopyrimidines (TP) can best be observed in the case of OT due to their thermal properties and the size of the nanostructures formed.Their supramolecular assembly formation in PS leads to strongly increased dynamic moduli and a network-like behavior. The latter can be easily observed in the terminal flow regime. A minimum content of about 3 wt % is required for these effects. For lower concentrations the tectons do not organize and act as solvent. Thus, the corresponding curves lay below that of the neat matrix.

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10.1021/ma0211333 CCC: $25.00

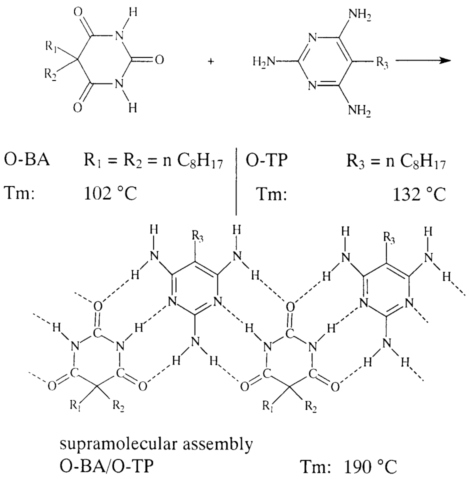

Figure 1. Assembling of BA (barbituric acid)-based and TP (2,4,6-triaminopyrimidine)-based tectons to the corresponding supramolecular structure. T_m indicates the melting temperatures of the individual tectons and of the equimolar compound.

In the case of the more polar PMMA as matrix, a similar solvent effect was observed for all concentrations. A self-organization could not be detected rheologically.[9] Obviously, enthalpic interactions between the matrix and the tecton are of key importance as it was found for the DBS tectons with several matrices.[10]

There are also a few papers[3,11] reporting the nonlinear viscoelastic properties of tectons in polymer melts. Common to all compounds is their extreme shear sensitivity, resulting in very low critical deformations (in the range of a few percent). From the structural point of view this fact is associated with the breakdown of network structures. A quantitative analysis of nonlinear behavior has not been reported so far.

The objective of the research presented here is the investigation of the nanostructure formation via supramolecular self-assembly of octyl-substituted barbituric acid (O-BA) and octyl-substituted 2,4,6-triaminopyrimidine (O-TP) in polypropylene. We compare the results with data on structure formation of tectons under investigation in PS and PMMA matrices to generalize the observed effects. Additionally, we clarify the role of tacticity for structure formation and therefore compare the rheological properties of compounds made of isotactic polypropylene (iPP) and atactic polypropylene (aPP). Special attention is paid to the quantitative investigation of nonlinear viscoelastic properties.

Experimental Section

Materials and Preparation. Both TP- and BA-based tectons are readily available as described previously by Bauer et al.[8] For our investigations we have chosen the octyl-substituted tectons (O-BA and O-TP) because their supramolecular assemblies readily melt around 170 °C (see Figure 1), a temperature which is favorable for rheological experiments with PP compounds.

The isotactic polypropylene (iPP) Novolen M was prepared by Targor/BASF AG in a metallocene-based process and was used without further purification. ^{13}C NMR spectroscopy revealed an isotacticity of mmm = 94.1%. The melting temperature is 140 °C as determined by DSC at a rate of 10 K/min.

The atactic polypropylene (aPP) JS38 was prepared in our laboratory by metallocene-catalyzed synthesis.[12] The relevant properties of both matrices are given in Table 1.

Table 1. Properties of the Different Matrices

polymer	abbreviation	M_w (kg/mol)[a]	M_w/M_n[a]	$\eta_{0,190°C}$ (Pa·s)[b]
iPP	Novolen	267	2.0	4900
aPP	JS38	148	1.9	1700

[a] High-temperature GPC, PP standard. [b] Measured with RMS800.

Compounds of iPP with the appropriate amounts of a 1:1 mixture of O-BA and O-TP (OT) were prepared in a Daca twin-screw microcompounder at 60 rpm and a processing temperature of 220 °C. The residence time in the compounder was about 5 min. The extruded materials were subsequently compression-molded under vacuum at 220 °C for 15 min, yielding specimen with a diameter of 25 mm and a thickness of 1 mm. A concentration series for the iPP matrix was prepared with $c_T = 1, 2, 3, 5$, and 10 wt % OT. The matrix of pure iPP was used as a reference. These samples are named iPPOT*X*, with *X* being the weight percentage of the added tecton mixture.

One compound of aPP with 5 wt % of an 1:1 mixture of O-BA and O-TP (aPPOT5) was made from a solution of all components in chloroform by precipitation in methanol followed by drying and compression-molding.

Rheological Characterization. The dynamic storage modulus G' and loss modulus G'' in shear were determined on a Rheometrics RMS-800 rheometer in parallel plate geometry under a nitrogen atmosphere. The rheological experiments include temperature ramps, frequency, and strain-sweep tests. Since the samples with a supramolecular structure showed pronounced nonlinearity and complex thermorheological behavior, a distinct measuring sequence was applied in all cases. The samples were loaded into the rheometer at 200 °C and equilibrated for 5 min at this temperature to provide melting of any superstructure and therefore erasing the thermal history. After establishing stationary conditions, a temperature ramp was conducted from 200 to 150 °C. Starting with this latter temperature, a full temperature cycle was run at a rate of 1 K/min up to 200 °C and back to 150 °C. If, as shown in Figure 2a, the first cycle led to full recovery of the initial state, then the second cooling was not carried out. In the case of the aPPOT5 sample the second cooling was run down to 40 °C. The changes in material properties were followed by measuring the dynamic moduli at a frequency of 1 rad/s. Subsequently, frequency sweeps were taken every 10 deg after time sweeps have proven to yield constant moduli. For these tests, identical and minimal deformations were chosen, i.e., generally between 0.6 and 1%.

In addition, deformation-dependent test were conducted applying a constant frequency of 1 rad/s at a temperature of 150 °C, varying the deformation between 0.4 and 500%. For these tests samples have been used which were equilibrated as described above.

The creep behavior of some samples was determined at a temperature of 150 °C using a CVO Bohlin rheometer. Prior to the creep tests, the above-mentioned thermal treatment was applied to the samples.

Results

Thermorheological Properties and Self-Assembling. The formation of supramolecular assemblies by self-organization of tectons within the polypropylene matrix can be nicely followed by shear rheological measurements. First, we consider the initial temperature sweeps at constant frequency across the melting point of the assemblies similar to DSC experiments. This is shown in Figure 2a, where the rheological responses of the neat matrix and an iPP compound containing 5% tecton are given together with the temperature profile. Comparing the moduli at the beginning and the end of the cycle, one can easily recognize the reversibility of the structural changes in the material. The strong increase of moduli at about 2000 s is associated with the buildup of an internal structure

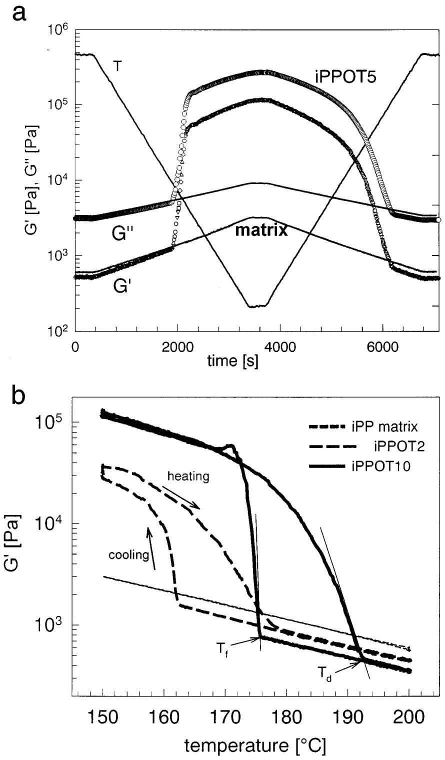

Figure 2. (a) Storage (G') and loss (G'') moduli during a time-resolved temperature cycle 200 → 150 → 200 °C (1 K/min, 1 rad/s) for iPP matrix and the compound containing 5 wt % OT (iPPOT5). (b) Storage (G') and loss (G'') moduli during a temperature cycle 150 → 200 → 150 °C (1 K/min, 1 rad/s) for the iPP matrix and the compounds containing 2 and 10 wt % OT (iPPOT2 and iPPOT10). T_f and T_d indicate the beginning (formation) of self-assembling upon cooling and the end of structure breakdown (destruction) upon heating, respectively.

while the slighter and longer lasting decrease of the moduli to values below the neat matrix is accompanied by the dissolution of this structure. The presentation of these data in dependence of the temperature makes it possible to analyze transition temperatures more precisely. This is shown in Figure 2b where the temperature dependence of the storage modulus G' between 150 and 200 °C for the pure iPP matrix and for two compounds containing 2 and 10 wt % of OT is given. Other concentrations were omitted for reasons of clarity. Because of the fact that structural changes associated with elastic and viscous properties of the compounds are similar (see Figure 2a), we concentrate on the analysis of G' data. Only if viscous properties have to be analyzed separately will we add this information.

From the temperature cycles several findings can be made: In contrast to the pure iPP matrix, the compound with 10 wt % OT reveals identical moduli during heating and cooling only below 170 °C and above 192 °C. In between, the moduli of the heat-up are substantially higher than during cooling, and a noticeable hysteresis can be observed. The significantly increased moduli of the compounds in comparison to the matrix at low temperatures indicate structure formation by assembling of the tectons. At high temperatures this process reverses to a dilution effect. In the latter case the tectons are disassembled and act as solvent, and consequently, the modulus is substantially lower than that of the neat matrix. In the iPP compound containing only 2 wt % OT, both effects are less pronounced and the hysteresis is smaller. For the 1% sample (not shown here) no structure formation can be detected during this cycle.

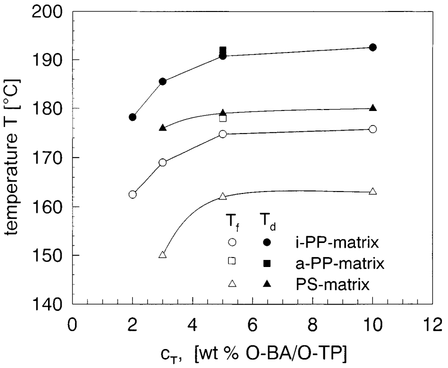

Figure 3. Values of T_f (structure formation temperature upon cooling) and T_d (structure melting temperature upon heating) in dependence of the content of OT in different matrices.

From the intersection of tangents shown in Figure 2b for the sample iPPOT10, it is possible to determine two characteristic transition temperatures, i.e., 193 °C upon heating (the dissolution temperature of the internal structure, T_d) and 176 °C upon cooling (the corresponding formation temperature, T_f). The transition temperatures of all samples under investigation together with those of the aPP-sample and PS-samples[9] are presented in Figure 3. The thin solid lines are drawn to guide the eye. For tecton concentrations, c_T, between 2 and 5% the transition temperatures change significantly while for higher concentrations this effect levels off. The transition temperatures for the 10% sample are in the range where the neat assemblies melt and form (see Figure 1). This behavior is similar to what we already observed for PS compounds.[9] The only difference is the absolute value of the transition temperature: The formation and dissolution temperatures of the assemblies are significantly lower in PS compared with PP.

Viscoelasticity and Sol–Gel Transition. Knowing in which temperature and concentration ranges OT organize to a superstructure, their dynamics can be probed by isothermal frequency sweeps, i.e., measurements of the dynamic moduli in dependence on the frequency at a given temperature. For these experiments we choose the smallest possible deformation amplitude, which gives a reliable torque signal. Later we will see that even this small deformation amplitude in the range of parts of a percent yields deformation dependent moduli and that the linear viscoelastic range is not accessible by this technique. Nevertheless, we use the oscillatory rheometry because it is the only method that allows analyzing the dynamics of the material without modifying it too much by shearing.

Essentially, we have to compare the frequency sweep of the compound with that of the matrix at given temperatures within the temperature interval of interest. This can be favorably done by analyzing the oscillatory data in the so-called vanGurp–Palmen plot (see Figure 4a,b). In this presentation the phase angle, δ, is plotted vs the reduced modulus, G_{red}, the absolute value of the complex modulus scaled with the plateau modulus (in our case PPs of different tacticity, for details concerning PP see Eckstein et al.[13]). This plot has the advantage that different isotherms fall on *one* curve without shifting if the time–temperature superposition principle (TTS) holds. Usually, this is the case for neat

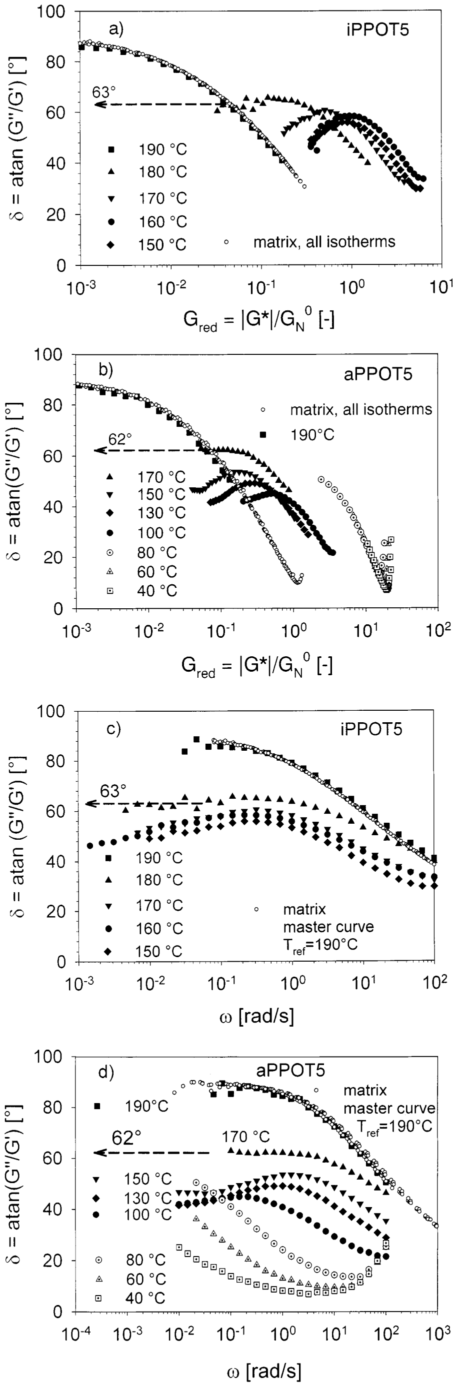

Figure 4. Reduced vanGurp–Palmen plot for (a) the iPP matrix and 5 wt % OT in iPP (iPPOT5) and (b) the aPP matrix and 5 wt % OT in aPP (aPPOT5). Additionally, for the purpose of comparison, plots (c) and (d) present the same data as (a) and (b) in dependence of the frequency.

polymers such as the matrix of our compounds. Accordingly, all isotherms fall on a common curve (see small circles in Figure 4a,b) while the curve for the matrix polymer in Figure 4c,d is the result of a shifting procedure. Using the δ vs G_{red} presentation, the curve starts at 90° for the smallest reduced moduli, indicating that the material is viscous. With increasing G_{red}, the phase angle decreases and the material becomes more and more elastic. For values of G_{red} around 1 (see now Figure 4b) the material is within its plateau region, and the minimum defines the plateau modulus (for details see Trinkle and Friedrich[21]). This region can be detected experimentally only for polymers that do not crystallize as the atactic PP used in this work. For G_{red} values higher than 1, the phase angle increases again and the material approaches the transition zone.

Moreover, in addition to a possible violation of TTS, the analysis of the vGP plot allows to detect transitions from a liquid to a solid. If a material approaches a phase angle of 0° at the smallest measured reduced moduli, this G_{red} value characterizes an equilibrium modulus due to cross-linking or other processes which turn a polymeric liquid into a solid. A constant phase angle different from 90° for the smallest G_{red} values is characteristic of a material at its gel point. In fact, this criterion was derived on the basis of phase angle–frequency data (see e.g. Winter and Mours[15]), but as can be easily recognized from the comparison presented in Figure 4a,c as well as in Figure 4b,d the used transformation of abscissa data leads only to a compression of the curve and does not change the characteristic angle.

Figure 4a shows the results of oscillatory measurements in δ vs G_{red} coordinates for iPPOT5 and Figure 4b for aPPOT5. Obviously, the most striking feature of the data shown in Figure 4a is the violation of TTS. While at 190 °C the tectons are completely dissolved in the iPP matrix and, consequently, their dynamics is entirely determined by that of the matrix, at lower temperatures a network effect is apparent. There are two attributes of this effect. First, with decreasing temperature the curves are shifted to higher moduli by more than 1 decade in comparison to the matrix. Second, most of the curves pass through a maximum and bend downward with decreasing G_{red}. An extrapolation to $\delta = 0$ of these data points gives a rough estimate of the equilibrium modulus of a tecton network (here between 1 and 10% of the plateau modulus of the matrix) formed during cooling. It will be shown later that the value of such an equilibrium modulus can be determined more precisely (at least for some of the compounds) on the basis of creep experiments. For small G_{red} values the data points of the isotherm corresponding to 180 °C form a plateau, which is additionally visualized by the horizontal dashed line. According to our analysis of the vanGurp–Palmen plot, this behavior can be identified with the gel point. Because of the fact that usually the gel point is determined in tan δ–ω coordinates and to show the differences between both ways of presentation, we added the corresponding Figure 4c,d. The comparison reveals that a plateau is easier to detect if the phase angle is presented in dependence of frequency. However, because of its advantage in analyzing additionally the thermorheological behavior, we prefer the presentation of loss angle vs the reduced moduli.

To check the validity of TTS at temperatures below 150 °C and to analyze a possible influence of tacticity on self-assembling and sol–gel transition, we present the corresponding data of compounds of the same tectons immersed in an atactic PP. Using aPP, we have eliminated the effects of matrix crystallization without changing the enthalpic interactions between the matrix and the tectons. These results are shown in Figure 4b. Because of the broader temperature interval available for measurements, we are able to capture the minimum in the master curve of aPP, which defines the plateau modulus of this material. The rheological response of aPPOT5 is similar to that of iPPOT5. Again, we observe dissolved tectons in the matrix at 190 °C and a gel point of 170 °C. As in the previous case, the dashed line

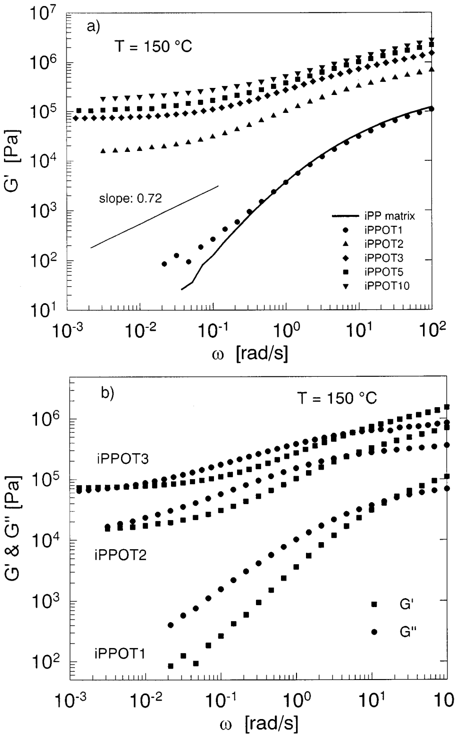

Figure 5. Isothermal ($T = 150$ °C) frequency dependence of (a) the storage moduli G' of iPP with 0, 1, 2, 3, 5, and 10 wt % OT and (b) the storage G' and loss G'' moduli of iPP with 1, 2, and 3 wt % OT.

represents an extrapolation of the experimental data (now with less scatter) to low values of the reduced modulus, which allows an easy estimation of the corresponding phase angle. For lower temperatures the same network effect can be detected as for the iPP sample: The curves bend downward for smallest G_{red} values and thus indicate the appearance of an equilibrium modulus, G_e. For both matrices, the TTS principle is violated in a wide temperature range. It is interesting to note that for deep quenches, $q = T_d - T > 100$ K, the single isotherms start to superpose and form a master curve. Moreover, these data indicate that the plateau modulus of the compound is approximately 20 times higher than that of the neat matrix.

Now we address the concentration dependence of the moduli of the compounds in a broad frequency range to answer the question in which concentration range the sol−gel transition can be observed for the deepest possible quench. Figure 5a depicts the concentration dependence of the storage modulus at a temperature of 150 °C, and Figure 5b shows the storage and loss moduli in the concentration range in which the sol−gel transition is expected. The samples containing 2% or more tectons (see Figure 5a) show a pronounced network behavior in the entire frequency range. The storage moduli are shifted significantly to higher values in comparison to the matrix. Moreover, a frequency-independent modulus, which is characteristic for solid-like behavior, builds up at the smallest frequencies. For the sample containing 1% tectons, features of structure formation are observed, too. At the smallest frequencies a slight increase in elasticity in comparison to the matrix can be detected.

Analyzing all data presented in this picture, a large gap between the curves for 1 and 2% is striking. This gap as well as the slopes of the adjacent curves at smallest frequencies implicate that the gelation of this system occurs at a concentration in between.

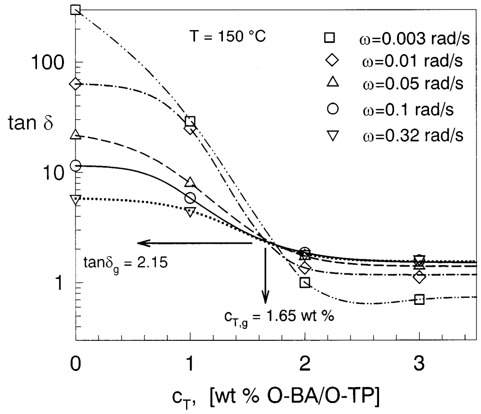

Figure 6. Loss factor, tan δ, vs concentration of equimolar mixture of O-BA/O-TP tectons in wt % for five different frequencies. The lines are drawn to guide the eye.

Prior to the determination of the gel concentration, we analyze in more detail the rheological changes of the compounds in this concentration region. From Figure 5b it can be clearly recognized that the rheological response of iPPOT1 resembles that of a neat polymer system in its terminal relaxation region: G'' is larger than G' left from the crossover point, and their ratio (= tan δ) increases with decreasing frequency. The compound containing 2% tectons already shows a second crossover of G' and G'' at the smallest frequencies, which is even more pronounced for the sample iPPOT3. For frequencies smaller than this crossover frequency G' exceeds G'', thus indicating the solidlike behavior of these compounds. Obviously, this transition, which we identify with the sol-to-gel transition, emerges in the concentration range between 1 and 2% tectons. To determine the exact gelation concentration, $c_{T,g}$, alternatively, we follow a procedure outlined by Aoki et al.[14] Accordingly, this concentration can be determined if one plots the tan δ values determined at different, as small as possible frequencies vs the concentration. Figure 6 presents the results for five frequencies in the range 0.32−0.003 rad/s. Because of the fact that the tan δ values of the iPP matrix and iPPOT1 for the smallest frequency ($\omega = 0.003$ rad/s) were not experimentally available (see Figure 5), we determined these values by linear extrapolation. In Figure 6 a sharp decrease of the tan δ can be observed if the concentration increases from 0 to 2% tectons. This decrease becomes sharper with declining frequency. For concentrations of 3% and higher the tan δ values remain almost constant. Only for the lowest frequency (here 0.003 rad/s) a decrease below 1 can be monitored. We suggest that a decrease of the tan δ values further below 1 could be observed only for frequencies smaller than 0.001 rad/s, a range which is not accessible with our instrument. Nevertheless, all these curves intersect in one point (see arrows) which determines the sought gel concentration for this system: $c_{T,g} = 1.65\%$. From the characteristic tan $\delta_g = 2.15$ ($\delta_g = 65°$) the slope of the corresponding G' curve (power law type) can be identified to 0.72. This value is typical for physical gels (see e.g. Winter and Mours[15] or Aoki et al.[14]), and a corresponding curve with this slope is shown in Figure 5a.

Nonlinear Viscoelasticity. All measurements analyzed so far were taken at the smallest possible, constant deformation of about 1%. To analyze how the

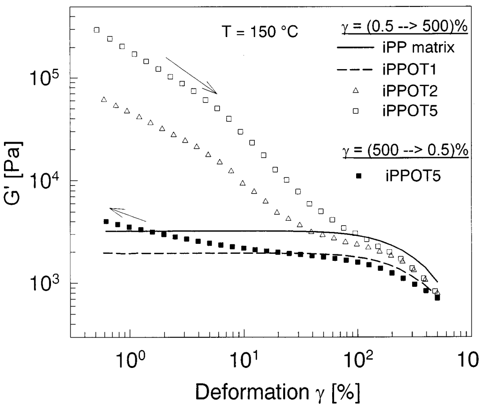

Figure 7. Storage modulus for the iPP matrix and samples containing 2 and 5 wt % tecton (iPPOT2 and iPPOT5) in dependence of oscillatory shear amplitude. The hollow symbols indicate the modulus course during increasing amplitudes and the filled symbols during decreasing amplitudes after the maximal deformation was reached.

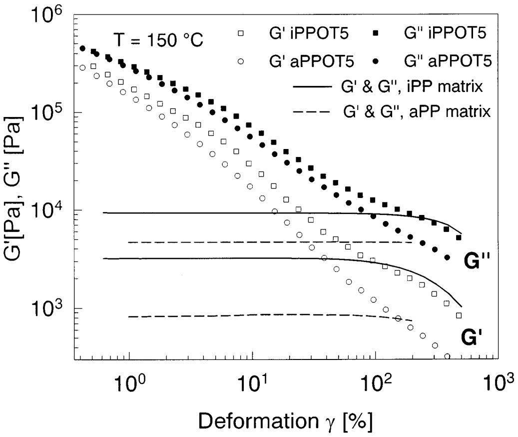

Figure 8. Storage (G') and loss (G'') moduli for the iPPOT5 and aPPOT5 together with their matrices in dependence of oscillatory shear amplitude. The deformation was increased from its lowest to its highest value.

viscoelastic properties change with increasing deformation amplitude, we turn to strain sweeps. Afterward, we will estimate at least for one particular sample the critical deformation for which the rheological behavior becomes deformation independent.

Strain sweeps at a constant frequency of 1 rad/s and a constant temperature of 150 °C were performed on all PP compounds. The resulting curves are shown in Figure 7 for the iPP matrix as well as for samples with 1, 2, and 5% tectons. In Figure 8, a comparison between both matrices is presented for the samples containing 5% tectons. The linear viscoelastic behavior of the neat iPP matrix (see bold solid line in Figure 7) can be observed up to deformations of about 100%. At higher deformations the storage modulus becomes strain dependent and decreases with increasing deformation. The curve of iPP with 1 wt % OT reveals the same shape as the curve of the neat matrix but is slightly shifted to lower moduli, as the tectons mainly act as a solvent. For tecton concentrations of 2 wt % and higher the behavior changes completely. In fact, measurements in the linear viscoelastic region cannot be realized with this technique. A decrease of the storage moduli with increasing deformation starts right from the beginning at smallest deformations. At the highest deformations between 100 and 500% the values become lower than those of the neat matrix. An explanation of this effect will be given later in the discussion part of this paper.

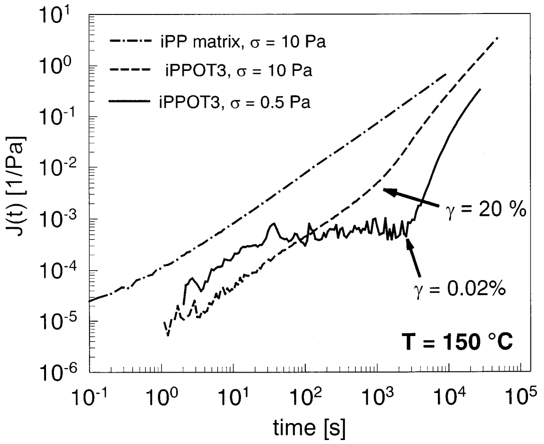

Figure 9. Shear creep compliance, $J(t)$, for the iPP matrix and the sample iPPOT3 at different shear stresses σ.

Another aspect, which has to be addressed, is related to the reversibility of the structural changes during the application of varying strains. The filled squares in Figure 7 indicate the modulus course of the sample containing 5% of tectons at decreasing strain amplitudes after the sample has experienced the maximum deformation of 500%. The storage modulus slightly increases with decreasing deformation amplitude, but the recovery is very limited. It can be doubted that the initial modulus will be reached in conceivable time under the given conditions.

The same nonlinear behavior can be found for self-assembled tectons in aPP (see Figure 8). One immediately recognizes that the dynamic moduli of both samples have roughly the same value at the smallest accessible deformation amplitudes. With increasing deformation the moduli decrease and fall below the values of the corresponding moduli of the two neat matrices, a behavior we have already seen in Figure 7. Moreover, the ratio between G'' and G', i.e., the tan δ value, becomes larger with increasing deformation amplitude. This behavior—a "liquidifaction" of the sample due to shearing in the nonlinear regime—allows us to explain why the tan δ values of the samples in the gel state as analyzed in Figure 6 do not fall significantly below tan δ_g. We can assume a concentration-dependent characteristic deformation, at which the sample's behavior becomes linear. This deformation shifts with increasing content of tectons to smaller values, and as a consequence, our oscillatory experiments at a fixed deformation fall in different ranges of each sample's nonlinearity zone.

The differences between the moduli of the neat matrices are due to their different molecular weights. However, it has to be emphasized that the differences between both compounds disappear under deformation conditions for which the influence of the matrix can be neglected, i.e., for the smallest deformations. In conclusion, we can state that the technique of amplitude sweeps is not appropriate to establish a critical deformation below which linear behavior is present.

Finally, the critical deformation for the sample iPPOT3 should be estimated using a creep technique. Only for the compound containing 3% OT creep curves could be recorded at a sufficiently low stress level, permitting the determination of the critical deformation. Figure 9 shows the creep curves of iPPOT3 measured at two stress levels together with the curve of the neat matrix. While the curve for the matrix represents the expected response of a linear polymer (the derived zero shear viscosity is of about 14 kPa·s and corresponds to the value measured by dynamic rheology), the compound reveals much smaller values of the creep compliance $J(t)$ at all times of the experiment and, depending on the stress level, σ, different behavior at short and intermediate times. The sample iPPOT3 measured at $\sigma = 10$ Pa shows flow behavior (the slope of the curve is about 1) up to 1000 s, which corresponds to an experienced deformation of about 20%. This is followed by a strong increase of $J(t)$. The same sample measured at 0.5 Pa over a long period shows the response of a viscoelastic solid whose compliance levels off at a value corresponding to a deformation of about 0.02%. The solidlike behavior disappears after approximately 3000 s, and a rapid deformation process sets in, leading to compliances similar to that of the matrix.

Discussion

From the literature[8,9] we know that equimolar mixtures of OT crystallize and melt at temperatures around 170 and 190 °C, respectively. These characteristic transition temperatures and the morphology of the samples are strongly influenced by the presence of a solvent (here polymer; for details see Guenet[16] and Terech and Weiss[2]).

From the comparison of rheologically determined transition temperatures of OT in PS with those determined in DSC experiments (see Fuchs et al.[9]), we know that the characteristic temperature upon heating, T_d, can be identified with the end of the dissolution of the assemblies, while T_f marks the begin of the structure formation upon cooling. This is confirmed for the assembly of OT in PP matrices, too. The temperatures T_f and T_d mark an interval where hysteresis effects are pronounced, and the rheological response of the material depends on the sign of the heating rate (i.e., heating or cooling).

From our previous work on dibenzylidene sorbitols (DBS) dissolved in poly(propylene oxide)[6] (PPO), we know that the enthalpic interactions between matrix and tecton significantly influence the transition temperatures. This is the case for the tectons used here: Comparing the characteristic temperatures of PS and PP shown in Figure 3, we can state a lowering of T_f and T_d with increasing polarity of the matrix polymer. For PMMA, no assembling is observed in the entire concentration range of interest.[9]

The concentration at which the self-organization of tectons is rheologically detectable also depends on enthalpic interactions. While the least polar polymer has the smallest concentration (2% for PP), the more polar PS requires a higher concentration (about 3%), and for the most polar polymer, PMMA, self-assembling could not be detected in the concentration and temperature ranges of interest. This result is in agreement with our findings for DBS compounds.[6] For the latter a quantitative correlation between the transition temperatures and the enthalpic interaction energies between tectons and matrix expressed in terms of Hildebrand's solubility parameters has been verified. For the samples presented here this quantification cannot be tested due to the missing Hildebrand parameters of O-BA and O-TP. Nevertheless, we conclude that similar to DBS the structure formation in the compounds under investigation is controlled by enthalpic interactions, too. Obviously, the larger the difference in the solubility parameters of tecton and polymer (in the order: PP > PS > PMMA) is, the smaller the depression of transition temperatures (T_f and T_d) in comparison to the neat tecton.

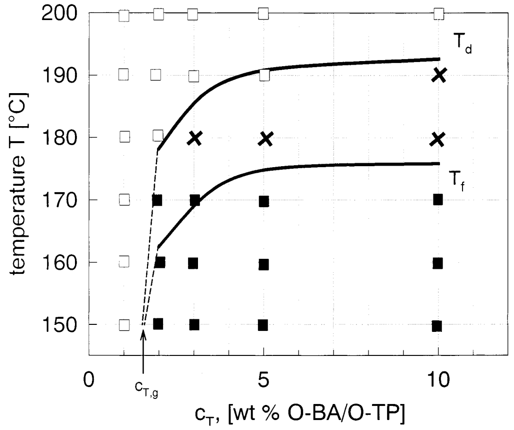

Figure 10. Rheological state diagram for all iPP/tecton samples. The open squares characterize the pregel state, the closed squares the postgel state, and the crosses those samples that are at the gel point. For details see the text.

From Figure 3 it can also be recognized that no significant differences exist between the transition temperatures of isotactic and atactic polypropylene compounds. This fact emphasizes the importance of enthalpic interactions and points out that intrinsic chain properties like chain flexibility are not relevant for the characteristic temperatures.

Now, we discuss the question at which temperature the self-assembling process of a given sample has proceeded so far that the formed second phase causes a sol−gel transition. To this end we use the frequency sweeps of all isotactic samples in the covered temperature range (see e.g. Figures 4a and 5 for $T = 150$ °C). If we assume that for the smallest G_{red} values the tan δ curves have a negative slope for a sample in the sol state, a slope of about zero for a sample at the gel point, and a positive slope for a compound in the gel state, then we can construct a state diagram as is given in Figure 10. In this diagram the characteristic temperatures together with gel-point concentration as determined by the Aoki method are incorporated.

Figure 10 shows that for the 1% sample no sol−gel transition can be detected in the given temperature range. Nevertheless, with decreasing temperature the self-assembling of tectons is in different states. While at 190 °C the moduli of this sample are smaller than that of the matrix in the whole frequency range, at 150 °C the storage moduli exceed the matrix values at smallest frequencies as can be recognized from Figure 5a. For the 2% sample the self-assembling process must be accompanied by the sol−gel transition in a small temperature interval between 180 and 170 °C (see Figure 10). For higher concentrations the gel point characteristic (see the crosses) can be detected over a broader temperature range. We assume that the range between T_d and T_f marks that temperature interval in which the sol-to-gel transition occurs, and their extrapolation to smaller concentrations is given by the dashed lines. The only exception from this rule, the sample

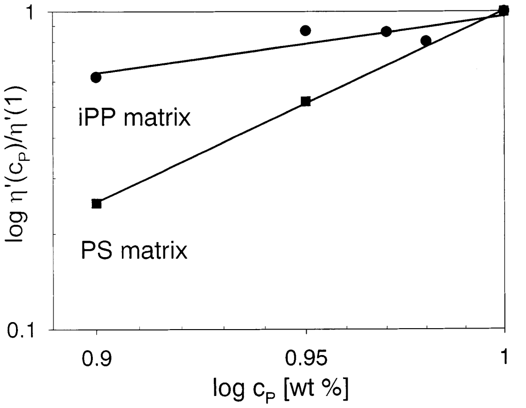

Figure 11. Relative dynamic viscosity determined at a frequency of $\omega = 0.02$ rad/s of iPPOT and PSOT (see ref 9) series at 190 °C in dependence on the polymer concentration c_P.

iPPOT2 at 170 °C, can be explained on the basis of the different frequencies by the help of which the different data points, symbols and lines, have been determined. If the frequency sweeps had been recorded only down to 1 rad/s, we could not decide whether the sample is in the gel state or not at this temperature.

Now we turn to the discussion of the validity of the time−temperature superposition principle for tecton networks in both PP matrices for the example of 5% samples. The data presented in Figure 4a,b reveal that this principle is violated for both iPP and aPP samples because the isotherms do not merge in a single master curve. The same behavior was found for the tectons in PS (Fuchs et al.[9]). The forms of the individual isotherms as well as their position in the plot are roughly the same for both matrices, indicating no significant differences between the samples made of iPP and aPP. This observation is verified by our measurements presented in Figure 8. The behavior of both samples at the smallest deformations clearly reveals a matrix-independent material response. The analysis of all these data brings us to the conclusion that no differences exist between the tecton networks formed in different PP matrices concerning their thermorheological properties. This behavior of the tectons in PP is qualitatively similar to results obtained with DBS in iPP:[10] In the accessible temperature range the violation of the TTS principle is the rule for this class of materials at least in the vicinity of the transition temperature. For deep quenches of 100 K and more, however, the TTS principle seems to hold for aPP samples as can be recognized from Figure 4b. In this temperature range the self-assembling process is finished, as all tectons are incorporated in a heterogeneous network structure of unknown topology. Under these conditions the thermorheological response of the samples is governed by that of the matrix.

In the following we discuss the concentration dependence of the rheological properties of tectons in iPP matrix at two different temperatures. First of all, we analyze the rheological state of compounds at 200 °C where the tectons are dissolved and influence the rheology of the matrix like a solvent. In Figure 11 the viscosity determined from the G'' data at the smallest accessible frequency is plotted vs the polymer concentration. Supplementary, we added the corresponding data for the tectons immersed in PS.[9]

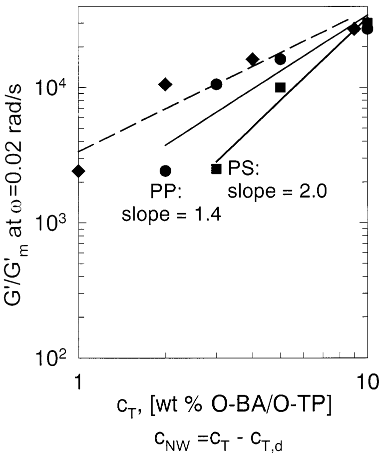

Figure 12. Relative storage modulus determined at a frequency of $\omega = 0.02$ rad/s for iPPOT (○) and PSOT (□, see ref 9) series at 150 °C in dependence on the tecton concentration c_T and on the concentration of tecton incorporated into the network, c_{NW}, in the case of PPOT (◇). $c_{T,d}$ is the amount of tectons remaining dissolved for all samples.

According to Ferry,[19] the viscosity decrease of a polymer solution due to the addition of solvent can be described by the following equation:

$$\eta_0 = \eta_{0\mathrm{matrix}} a_c(\phi)\phi^{3.5} \qquad (1)$$

In this equation, $\eta_{0\mathrm{matrix}}$ is the zero shear viscosity of the neat undiluted polymer (in the figure designated as $\eta'(1)$) and ϕ the polymer volume fraction. Here we can use c_P (the weight fraction of polymer, $c_P = 1 - c_T$) and ϕ synonymously because the density of OT is close to 1. The second term on the right-hand side of eq 1 accounts for effects associated with the interaction between solvent and polymer, leading to a change in free volume or, correspondingly, changes in the monomeric friction coefficient of the polymer. If these changes do not occur during dilution, a_c is a constant. The third term reflects the change in entanglement density due to dilution. Plasticizing effects are not included and not relevant because no shift of the glass transition temperature is observed for the compounds (for PS see Fuchs et al.[9]). The analysis of corresponding PP data presented in Figure 11 reveals a slope of about 4, a value close to 3.5, which can be interpreted on the basis of an almost ϕ-independent a_c term and the entanglement scenario. Because of the obviously weak interactions between the tectons and the apolar matrix, the entanglement dominated viscosity change is reasonable.

The situation changes completely in the case of the PS matrix. The high slope of the curve (around 14) in Figure 11 can hardly be explained by entanglement effects solely. In contrary, there are known polymer/solvent systems for which the a_c term has a much stronger concentration dependence than the entanglement part, and very often an exponential dependence is observed.[19] Because of the fact that the slope is mainly determined by the a_c term ($a_c \propto \phi^{10.5}$), we conclude that free volume effects are dominating in the case of PS OT interactions.

The analysis of the concentration dependence of the storage moduli at 150 °C (see also Figure 5) is given in Figure 12. Again, the network formation in PP and PS is compared. In this picture we analyze the moduli at smallest frequencies, i.e., 0.02 rad/s for PP and 0.001 rad/s for PS (for details see Fuchs et al.[9]). To exclude the influence of matrix' elasticity (the storage modulus of the compound is a combination of the matrix modulus and the modulus of the network formed by tectons), the relative moduli are plotted. For the concentrations where a network of tectons is present (2% and higher for PP and 3% and higher for PS), a remarkable reinforcement effect can be detected. The relative moduli of both systems are in the range of 10 000 and more. With increasing tecton concentration the differences between compounds of different matrices diminish. Obviously, networks formed in both matrices display no significant differences. We argue that the properties of the network formed in both matrices are similar.

Finally, there is another aspect, which we have to discuss. From the deformation sweeps presented in Figure 7 we know that all curves for samples with 2% and more tecton merge with the 1% curve at the highest deformations. This fact can be explained only if we assume that an amount of tecton of about 1% remains dissolved in all samples. Obviously, the 1% sample is the material, which constitutes the effective matrix for all other compounds with higher tecton concentrations. Consequently, concentrations have to be corrected in the following way: $c_{NW} = c_T - c_{T,d}$, where $c_{T,d}$ is the concentration of tectons that remain dissolved in all PP samples and c_{NW} that part of tectons which build up the network structure. The corrected data are given in Figure 12 by the diamonds; the linear regression yields a slope of about 1. A similar correction should be performed for tectons in PS matrix, but we do not have the necessary data for the determination of $c_{T,d}$ in the case of PS. Nevertheless, a correction would lead to a curve with a slope smaller than 2. A quantitative discussion of these results on the basis of network models (see e.g. Jones and Marques[20]) is not the objective of this paper, and moreover, the application of these models asks for details of the network topology, which we do not have.

Conclusions

Small amounts of complementary tectons like the presented octyl-substituted barbituric acid (O-BA) and 2,4,6-triaminopyrimidine (O-TP) already have the potential to form superstructures by self-assembling in polymer matrices. We have investigated the effects of the structure formation within isotactic and atactic polypropylene matrices by dynamic-mechanical spectroscopy and compared the results with those obtained recently for the structure formation of these tectons in PS and PMMA.

We found drastically increased dynamic moduli in compounds with an OT content of 2 wt % and higher. The network effect due to the self-assembly of tectons reverses to a dilution effect well above 171 °C, which corresponds to the melting point of the neat assembly. The exact temperature, where this effect occurs, depends on the chemical nature of the matrix and the concentration of tecton, but not on the tacticity of the matrix polymer. We conclude that the enthalpic interactions between matrix and tecton are the most important factor controlling the network formation.

The unknown network structure formed as a result of self-assembling of the tectons is extremely fragile. A critical deformation of the compounds in the range of 10^{-4} is a first proof of their extraordinary shear sensitivity.

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft (DFG) through the SFB428 is gratefully acknowledged. The authors thank Dr. T. Bauer for making the tectons available.

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MA0211333