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Nanostructure Formation via Association of Tectons in Amorphous Polymer Matrices

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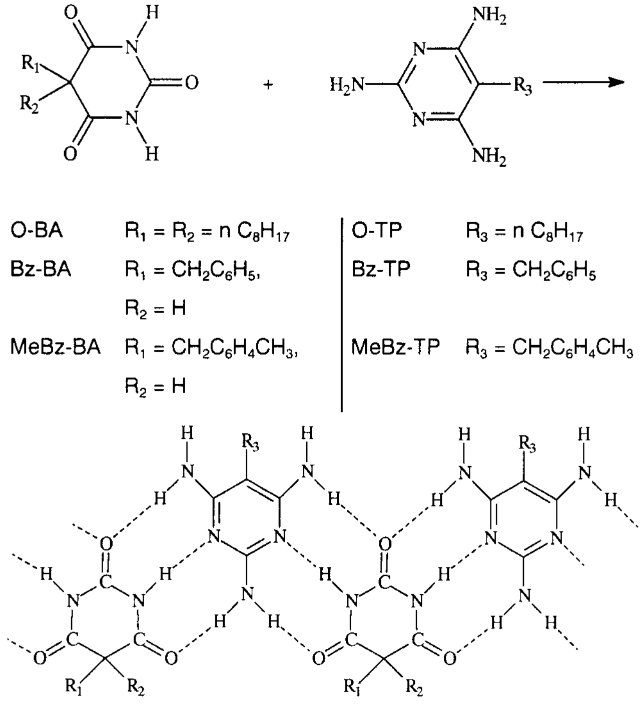
ABSTRACT: The supramolecular assembling of small amounts of octyl- and benzyl-substituted complementary tectons based upon barbiturates (BA) and 2,4,6-triaminopyrimidines (TP) was studied in a polystyrene matrix by means of differential scanning calorimetry (DSC), dynamic-mechanical spectroscopy, and transmission electron microscopy (TEM). Self-organization of these tectons within the compounds drastically changes the melt rheology in comparison to the pure matrix. Depending on external conditions such as temperature and mechanical deformation, the formation of BA/TP assemblies in polystyrene via self-organization leads to strongly increased dynamic moduli and a networklike behavior. A minimum content of 3 wt % of BA/TP is required for these rheological effects. A similar self-organization and reinforcing effect could not be observed in a more polar poly(methyl methacrylate) matrix. The resulting BA/TP structures were also examined by TEM and polarized light microscopy in both polymer matrices as well as at the interface of sandwiches consisting of PMMA and polystyrene layers. The microscopic techniques confirm the rheological results with respect to the dynamic self-organization and provide information about the concerning morphology development.

Introduction

New developments of nanostructured polymeric materials are highly stimulated by recent innovations in supramolecular chemistry and its novel approach to complex molecular and supermolecular architectures. The exciting potential of supramolecular self-assemblies leading to programmed supramolecular systems was reviewed by Lehn.[1] Supramolecular self-assembly is based upon the spontaneous recognition-driven association of small molecules that have the function of supramolecular monomers. According to Wuest, these monomers represent “tectons”, i.e., “frameworks with sticky sites”.[2,3]

Supramolecular assemblies of tectons in a polymer matrix represent a recent development in this area. These polymer assemblies—unlike conventional polymers, which are built by covalent linking of monomers—can form linear, branched, cyclic, helical, fiberlike, ladderlike, gridlike, and sheetlike superstructures by exploiting the formation of hydrogen bridges between complementary donor/acceptor-type tectons. Several groups report the use of supramolecular assemblies to produce nanostructured gels in organic and aqueous media as revised by Terech and Weiss.[4]

Supramolecular nanostructure formation is of great industrial significance and plays a key role in the nucleation of polyolefine melt crystallization. For example, dibenzylidene sorbitol (DBS) and its derivatives are well-known nucleating agents and clarifiers.[5−10] Shepard and co-workers[6] described the gel formation via three-dimensional self-assembling of dibenzylidene sorbitol, leading to connected nanofibrils within the polypropylene matrix. Similar results for dibenzylidene sorbitol in a PEO matrix have been reported by Thierry and co-workers.[7] The finely dispersed fibrils serve as nuclei for the epitaxial ongrowth during the polymer crystallization.



O-BA	$R_1 = R_2 = n\ C_8H_{17}$	O-TP	$R_3 = n\ C_8H_{17}$
Bz-BA	$R_1 = CH_2C_6H_5$, $R_2 = H$	Bz-TP	$R_3 = CH_2C_6H_5$
MeBz-BA	$R_1 = CH_2C_6H_4CH_3$, $R_2 = H$	MeBz-TP	$R_3 = CH_2C_6H_4CH_3$

Figure 1. Supramolecular assembling of BA- and TP-based tectons.

Recently, we reported about investigations of nanostructure formation achieved by means of supramolecular self-assembly of tectons based upon substituted barbiturates (BA) combined with complementary derivatives of 2,4,6-triaminopyrimidines (TP).[11] Each molecule can form three hydrogen bonds with two complementary molecules and therefore self-organize into ribbonlike structures that exhibit a layered morphology (see Figure 1).[1,11] We have examined the self-assembly of equimolar mixtures of the tectons in the pure state as well as in organic media and in polymer melts as a

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Table 1. Melting Temperatures and Densities ρ of Tectons and Their Supramolecular Assemblies

				R_1R_2-BA		R_3-TP		assembly	
sample	R_1	R_2	R_3	T_m (°C)	ρ (g/cm^3)	T_m (°C)	ρ (g/cm^3)	T_m (°C)	ρ (g/cm^3)
O−BA/O-TP	n-C_8H_{17}	n-C_8H_{17}	n-C_8H_{17}	102	1.076	132	1.152	171	1.058
Bz-BA/Bz-TP	$CH_2C_6H_5$	H	$CH_2C_6H_5$	210	1.445	191	1.285	271	1.301
Bz-BA/MeBz-TP	$CH_2C_6H_5$	H	$CH_2C_6H_4CH_3$	210	1.445	208	1.292	269	1.285

function of the substitution pattern. Thus, we were able to establish a new class of two-component nucleating agents for polypropylene where the nucleating efficiency is highly dependent on the substitution type and substitution pattern of BA and TP as well as on the interlayer spacings of the nucleating assemblies formed.

The objective of the research presented in this paper was the investigation of the nanostructure formation via supramolecular self-assembly of substituted barbituric acids (BA) and 2,4,6-triaminopyrimidines (TP) in the amorphous polymer matrices polystyrene (PS) and poly(methyl methacrylate) (PMMA). Special attention will be paid to the prerequisites for the structure formation, i.e., the matrix-assembly interactions, the concentration of the self-organizing tectons, and the processing history of the sample. Major tools for these investigations were dynamic-mechanical measurements in the melt, which made it possible to observe the different dynamic processes within the compounds and to vary the external conditions as temperature and mechanical stress. TEM and DSC were employed to investigate the underlying morphology and the thermal transitions of the tectons and their assemblies.

Experimental Part

A. Materials. Both TP- and BA-based tectons are readily available as described previously.[11] Similar to procedures reported by Bloomfield[12] and Beckhaus,[13] malononitrile was alkylated with alkyl halides in dry dimethyl sulfoxide (DMSO) using sodium hydride to generate the sodium salt of malononitrile. Monobenzylation was performed according to the Knoevenagel condensation using benzaldehydes, described by Milart,[14] followed by hydrogenation as proposed by Nanjo.[15] Formation of TP was achieved by reacting substituted malononitrile with guanidinium hydrochloride in dry ethanol similar to procedures reported by Russel and Hitchings.[16] The synthetic route to alkyl- and benzyl-substituted BA involved cyclization of the corresponding substituted diethyl malonate with urea, as proposed earlier by Fischer.[17]

The atactic polystyrene PS140 was anionically prepared by BASF AG and was used without further purification. The weight-average mass is 145 000 g/mol, and M_w/M_n is 1.02, respectively. The glass transition temperature is 110 °C as determined by DSC at a rate of 20 K/min. A methyl methacrylate monomer/polymer mixture (Acrifix 190) and a radically prepared PMMA modified for melt extrusion (Plexiglas 7N) with a weight-average molecular weight of 500 000 g/mol, and M_w/M_n of 2.40, were supplied by Röhm and used as received.

B. Polystyrene Compounds. Polystyrene compounds were prepared from ground pellets with the appropriate amount of an 1:1 mixture of BA and TP in a Randcastle Microtruder RCP MT 0250 single screw extruder with 30 rpm and processing temperatures between 210 and 230 °C. The residence time in the extruder was about 5 min. The extruded materials were subsequently compression molded under vacuum at 220 °C for 15 min. The obtained specimens for melt rheology appeared transparent with a slight yellow to brown color depending on the concentration and the substitution pattern of the tectons.

PS specimens for melt rheology investigations included 1, 2, 3, 5, and 10 wt % of O-BA/O-TP as well as 2 and 10 wt % of Bz-BA/Bz-TP. The matrix of pure PS140 was used as a reference.

C. PMMA/MMA and PMMA Compounds. BA and TP compounds for TEM investigations were separately dissolved in MMA/PMMA, poured together, and subsequently polymerized using dibenzoyl peroxide at 60 °C for 4 h. Excess MMA was then evaporated under vacuum at 80 °C for 10 h.

PMMA extruder compounds for the rheological measurements were prepared in a Randcastle Microtruder RCP MT 0250 single screw extruder with 30 rpm and processing temperatures between 220 and 240 °C.

D. Polymer Characterization. a. Thermal Analysis. Differential scanning calorimetry measurements were performed on a Perkin-Elmer DSC-7 at rates of 5 and 20 K/min between room temperature and 200 °C.

b. Density Measurements. Volumetric measurements were performed on microcrystalline samples using a Quantachrome micropycnometer working with helium gas.

c. Melt Rheology. The dynamic shear moduli G' and G'' were determined on a Rheometrics RMS-800 in parallel plate geometry under a nitrogen atmosphere. The rheological experiments included temperature ramps, strain sweeps, and frequency-dependent tests. Since the samples with supramolecular structure showed pronounced nonlinear, thermorheological complex behavior, a distinct measuring sequence was applied in all cases. After establishing stationary conditions in a time sweep at 150 °C, a temperature cycle was conducted from 150 up to 200 °C and back to 150 °C (160−220−160 °C for PMMA) at a rate of 1 K/min in the autotension mode, providing a constant gap. Subsequently, frequency sweeps were recorded at temperature intervals of 10 K after time sweeps have proven to yield constant moduli. For all tests, identical and minimal deformations were chosen, i.e., generally between 0.6 and 1%.

d. Polarized Light Microscopy. An Olympus Vanox AH2 research microscope with a Linkam THM 600/TMS 90 hot stage was used.

e. Transmission Electron Microscopy. TEM investigations were carried out with a Zeiss CEM 902 and a LEO 912 Omega microscope. To study the morphology of the assemblies in PMMA and PS, ultrathin sections (30−50 nm) were prepared at room temperature using a Reichert&Jung microtome equipped with a diamond knife. All the measurements were performed without staining.

Results and Discussion

Substituted barbituric acids, abbreviated as BA, and substituted 2,4,6-triaminopyrimidines, abbreviated as TP, were selected as complementary tectons because these components are known to form large and stable supramolecular assemblies by the formation of three H-bonds per molecule.[1,17] The individual tectons readily melt above the glass transition temperature of the amorphous PS or PMMA matrices, while the assemblies are still able to crystallize (see melting temperatures of components and assemblies in Table 1). Thus, a fine dispersion of the components should be achievable, and the supramolecular assembly might form from an isotropic, homogeneous distribution in the melt. A similar behavior is known for dibenzylidene sorbitol (DBS), an efficient gelator for low molecular liquids and well-known as a nucleating agent for polyolefins.[4,6−10] From scattering data and from microscopic investigations it was deduced that the high nucleating efficiency of DBS is on one hand due to its exceptional degree of dispersion in the isotropic molten polyolefin compound.

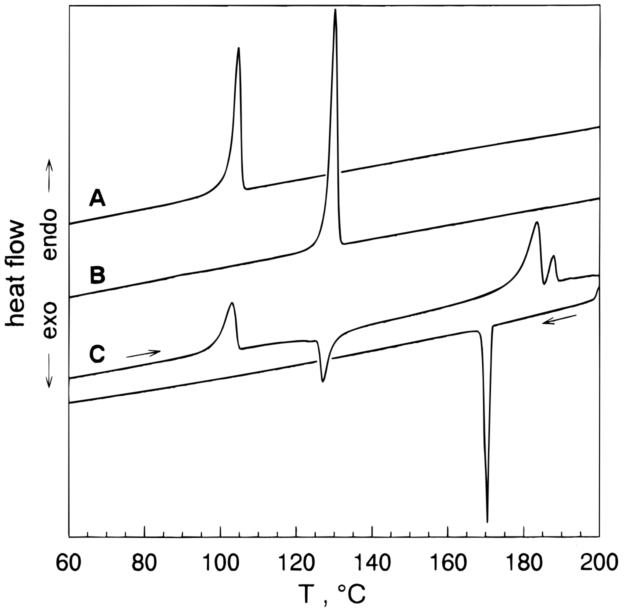

Figure 2. DSC heating traces (rate 5 K/min): (A) O-BA; (B) O-TP; (C) equimolar mixture of O-BA and O-TP together with subsequent cooling after 2 min at 200 °C.

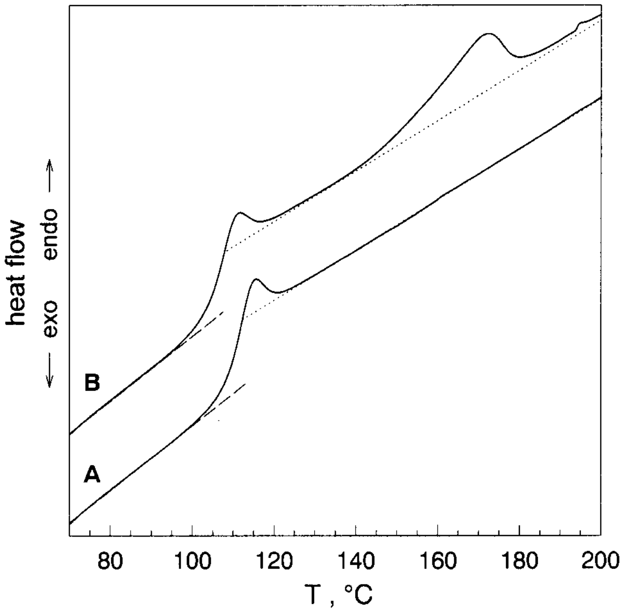

Figure 3. DSC traces of PS compounds at a heating rate of 20 K/min: (A) pure PS; (B) PS compound with 5 wt % of O-BA/O-TP assembly.

Upon cooling, on the other hand, DBS separates as a gel, thus forming a network of filaments, each of which behaves essentially as a continuous string of nucleation sites.[18] This self-organization has also been observed in viscous amorphous matrices as poly(dimethylsiloxane),[19] polystyrene,[20] or poly(propylene oxide).[21,22]

Polystyrene as an amorphous, thermally stable polymer matrix offers the advantage of a favorable temperature window for melt rheology investigations combined with excellent features for both TEM and polarized light microscopy. Furthermore, the anionic polymerization process yields narrow molecular weight distributions with a defined and well-understood relaxational behavior. This provides a reliable separation of the relaxation processes originating from the supramolecular structures and the matrix.

A. Self-Assembly of Tectons. The molecular structures of substituted BA and TP tectons and their supramolecular association are displayed in Figure 1. The melting temperatures of the tectons and the assemblies are listed in Table 1 together with their densities ρ. It is noteworthy that the supramolecular assemblies show substantially higher melting temperatures compared to those of the individual components due to the formation of three H-bonds per molecule.[11,17] The densities of the alkyl-substituted tectons and their assemblies are lower than in the case of benzyl substitution.

As shown previously, heating of an equimolar mixture of BA and TP tectons results in melting of the components and immediate formation of the corresponding assembly.[11] This can be monitored by DSC as shown in Figure 2. The pure tecton O-BA shows an endothermic melting peak at 102 °C, and O-TP melts at 132 °C. In the DSC trace of the tectonic mixture, melting of the O-TP is not visible, since it is covered completely by the simultaneous crystallization of the assembly. The endothermic signals at about 180 °C account for the melting and partially recrystallization of the assembly, until it is completely molten. The strong exothermic peak at 171 °C results from the recrystallization of the assembly upon cooling. The formation of the assemblies can also be monitored by FTIR, WAXS, and microscopic methods as described recently.[11,17,23]

Our former investigations have proven that the formation of superstructures takes also place at comparably low concentrations in a highly viscous polypropylene matrix.[11] Inspecting the DSC thermograms of the compounds in Figure 3, it is possible to retrieve characteristic processes of the pure tectons also in the PS matrix.

The thermograms in Figure 3 were recorded after the same thermal history, i.e., in the second run after cooling with 5 K/min from 200 °C, where the sample was annealed for 5 min. The melting temperature of the assembly within the PS matrix (thermogram B in Figure 3) is lowered and the respective DSC peak is broadened compared to the case of the pure assembly in Figure 2. Possible explanations are interactions between the tectons and the matrix thus disturbing the assembly crystallization or simply a changed morphology, i.e., smaller crystals with enlarged surface. The glass transition of the PS matrix in the compound appears also at a slightly lower temperature compared to that of the pure matrix. The broken lines in the glassy state and the dotted lines in the melt are all of the same slope, thus revealing that the heat capacities of the matrices remain unchanged upon addition of the assembly and that the viscoelastic softening behavior is dominated by the matrix.

B. PMMA/PS—Sandwich. The formation of the tectonic assemblies can also be visualized by investigating sandwich specimens. Figure 4 shows a light polarized micrograph of a three-layer sandwich originally prepared from two polymer films: a PMMA film containing 10 wt % Bz-BA and a PS film with 10 wt % MeBz-TP. The PMMA film was placed on the PS film, and the sandwich was annealed for 1 h at 220 °C. The two amorphous polymers are immiscible and hence appear dark in the polarized light. During annealing a third layer emerges at the interface of the polymers, now appearing bright due to its crystallinity. Obviously, this new layer is built up by the Bz-BA/MeBz-TP assembly that forms by migration of the respective tectons if the sandwich is heated above T_g of the polymers and above

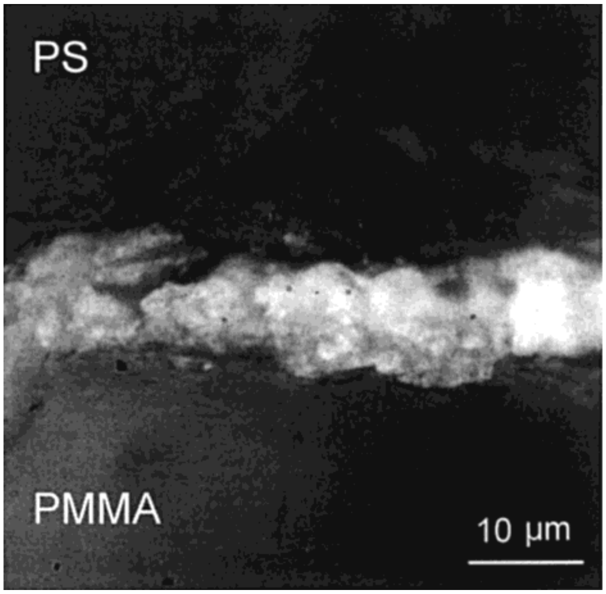

Figure 4. Polarized light micrograph of a PMMA/PS sandwich specimen after annealing for 1 h at 220 °C. Top layer (dark): PS with 10 wt % MeBz-TP; bottom layer (dark): PMMA with 10 wt % Bz-BA; intermediate layer (bright): crystalline layer of supramolecular Bz-BA/MeBz-TP assembly formed by migration of the respective components to the interlayer.

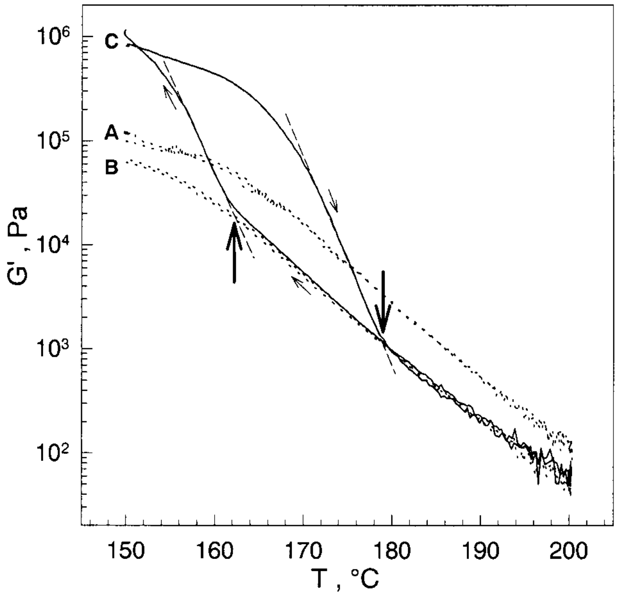

Figure 5. Temperature cycles 150 → 200 → 150 °C (1 K/min, constant frequency 1 rad/s) for (A) pure PS140, (B) with 5 wt % O-BA, and (C) 5 wt % O-BA/O-TP (solid line). The vertical arrows indicate the beginning of self-organization on cooling and the end of structure breakdown on heating.

the melting temperatures of the individual tectons. This shows the strong driving force for the formation of the supramolecular associates.

C. Rheology of Amorphous Polymer Matrices with Tectons. The findings from the DSC and TEM investigations presented below can be confirmed and extended by shear rheological measurements. First we consider the initial temperature sweeps at constant frequency across the melting point of the assemblies similar to the DSC experiments.

Figure 5 shows the temperature dependence of the storage modulus G' between 150 and 200 °C for the pure PS, a PS/O-BA/O-TP compound, and a compound with 5 wt % O-BA without its complementary tecton. The small arrows indicate the chronological sequence of heating and cooling. The loss moduli G'' are not shown here for clarity reasons but reveal the same qualitative picture with identical transition temperatures. From these temperature cycles several findings are possible: In contrast to the pure PS matrix, the compound with 5 wt % of the 1:1 O-BA/O-TP mixture reveals identical moduli during heating and cooling only above 179 °C. Below this temperature the moduli of the heat-up are substantially higher than during cooling, and a noticeable hysteresis can be observed. The moduli of the compounds at low temperatures indicate a reinforcing effect which reverses to a plastisizing effect at higher temperatures. In the PS compound containing only the single tecton O-BA, this plastisizing effect is predominant over the whole temperature range. This behavior is expected from the melting temperature of the pure O-BA (see Table 1) far below 150 °C, the lower limit of this rheological measurement. From the intersection of tangents shown in Figure 5, it is possible to determine two critical transition temperatures, i.e., 179 °C upon heating and 162 °C upon cooling.

In combination with the TEM and DSC investigations, these findings can be consistently explained with rigid supramolecular structures of crystallized assemblies from both tectons emerging above a certain concentration and below the mentioned critical temperatures. Thus, the critical temperature of 179 °C upon heating can be identified with the end of the melting of the assemblies (downward arrow in Figure 5), while 162 °C marks the beginning of the structure formation upon cooling (upward arrow). The area between heating and cooling cycle might serve as an estimate for the hysteresis of the self-organization. The presence of the single tecton O-BA does not lead to any reinforcing nanostructure formation in the covered temperature range.

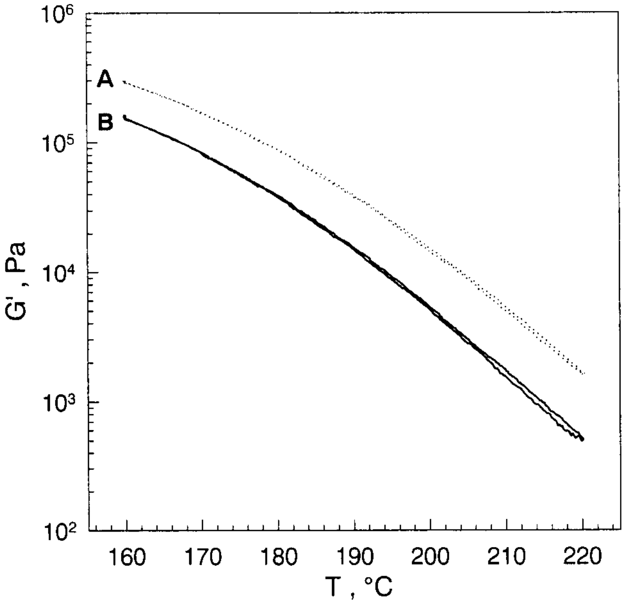

Figure 6. Temperature cycles 160 → 220 → 160 °C (1 K/min, constant frequency 1 rad/s) for extruded PMMA N7 with (A) 0 (dotted) and (B) 5 wt % O-BA/O-TP (solid line).

Figure 6 shows equivalent temperature cycles from 160 to 220 °C and back to 160 °C for a compound of extruded PMMA with 5 wt % O-BA/O-TP (solid line) in comparison to the pure PMMA matrix (dotted line). Here, the softening behavior of the compound is com-

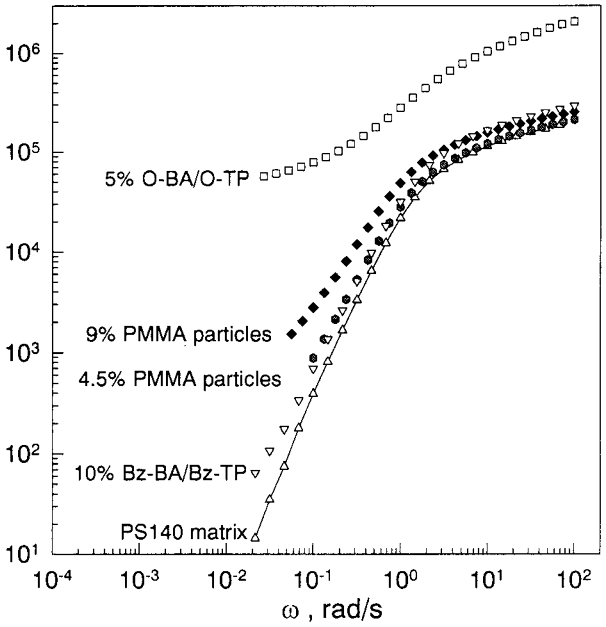

Figure 7. Storage modulus G' at 170 °C in dependence on the frequency for the pure PS matrix, the different compounds under investigation, and the same PS matrix filled with two different weight fractions of hard cross-linked PMMA particles (200 nm diameter).[24]

pletely reversible, and any transitions are not observed. Rather, a substantial plastisizing effect can be noted for the compound over the whole temperature range, i.e., also below the melting point of the pure assembly. Obviously, larger reinforcing assembly structures are not formed in PMMA above 160 °C, and a homogeneous molecular dispersed solution seems to predominate in this temperature range. Further cooling was not possible in the rheometer because of transducer limits, but also the TEM images at room temperature reveal a homogeneous sample without any superstructures. This can be explained with the polar character of PMMA, allowing the tectons to develop hydrogen bonds to the carboxylic functionalities of the matrix. This example demonstrates the importance of the balance between the matrix−tecton interactions and the matrix−assembly interactions for the self-organization. A certain degree of incompatibility for both interactions is one prerequisite for the structure formation within the matrix.

In Figure 7 isothermal frequency sweeps at 170 °C of PS compounds with 5 wt % O-BA/O-TP and 10 wt % Bz-BA/Bz-TP are compared to the pure matrix and the same matrix filled with two different amounts of spherical, cross-linked PMMA particles. On the condition that the assembly has formed completely, the weight percentage is equivalent to the volume content in the case of the O-BA/O-TP compound ($\rho_{PS} = 1.05$ g/cm^3). For the PMMA particle systems the volume contents are 4 and 8% ($\rho_{PMMA} = 1.19$ g/cm^3). The most striking effect is the strong increase in the storage modulus (and similarly in the loss modulus, not displayed here) of the O-BA/O-TP compound. At small frequencies, where the pure matrix has already reached the terminal flow region, this compound reveals the onset of a second plateau, typical for three-dimensional networks. It is obvious from the corresponding curves of the systems with hard, isolated PMMA particles that the reinforcement due to the assemblies goes far beyond the effect of a simple spherical filler. A possible explanation for these rheological features are particles with an exceptional aspect ratio, e.g. whiskers or platelets with a large surface. A similar rheological behavior with a strong increase of the elastic modulus in the low-frequency range has been found for exfoliated layered silicates in a PS matrix.[25] We addressed the problem of the underlying morphology by TEM investigations, which are presented below.

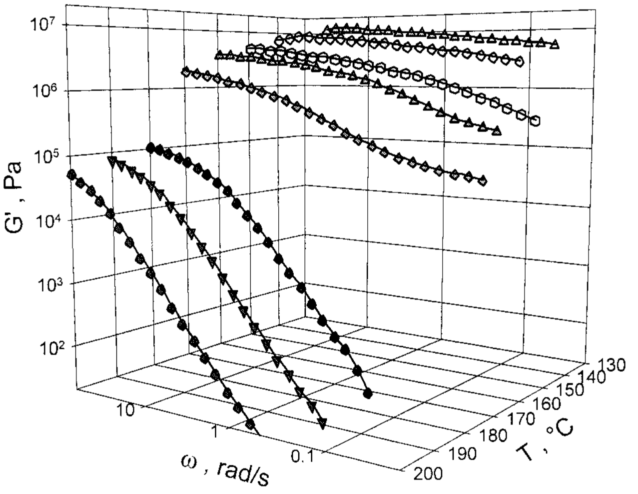

Figure 8. Isothermal frequency sweeps at different temperatures of the PS compound with 5 wt % O-BA/O-TP.

At first sight it might appear surprising that even 10 wt %, i.e., 8 vol %, of the benzyl-substituted assembly shows almost no reinforcing effect. From the DSC results and the TEM investigations, however, it becomes clear that the benzyl-substituted assembly has never come close to its melting point of above 270 °C during processing or measuring. Assembly structures, once formed, cannot reorganize and are too large and compact to give rise to an increase in the dynamic moduli.[26] The resemblance of the Bz-BA/Bz-TP compound with the particle-filled systems is therefore reasonable.

Figure 8 displays the frequency sweeps of the PS compound with 5 wt % O-BA/O-TP in temperature steps of 10 K. They were obtained after the initial heating/cooling treatment and after time sweeps at the given temperature resulted in constant G' and G'' values. What can be seen from this plot is first the large gap between the moduli of the isotherms from 130 to 170 °C on the one side and from 180 to 200 °C on the other. This distinguishes again the region with network behavior below 170 °C and the plastisized state above 180 °C. Second, it can be seen that the shape of the isotherms changes with temperature. Only slight differences are noticeable in the low-temperature region, probably due to minor morphological changes. The onset of the second plateau, however, completely disappears between 170 and 180 °C because of the breakdown of the superstructure. Thus, time−temperature superposition and the creation of master curves in principle are not possible for these structured samples. This fact again expresses the highly nonlinear, time- and history-dependent character of the compounds.

Nevertheless, utilizing the horizontal shift factors a_T of the pure PS matrix and adjusted b_T values, a superposition of the isotherms has been tried at the reference temperature $T_0 = 150$ °C. Figure 9 shows the result of this two-dimensional shift for the PS compound with 5 wt % O-BA/O-TP. The obtained horizontal and vertical shift factors, a_T and b_T, are compared to those of the pure matrix in Figure 10.

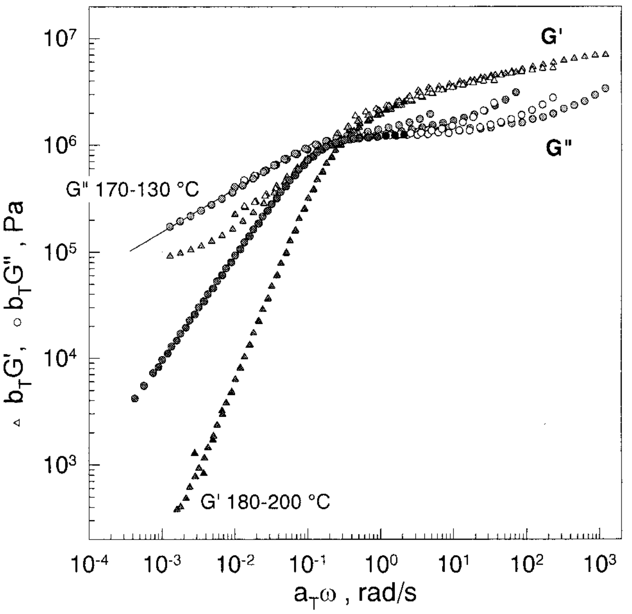

Figure 9. Attempt of superposing the frequency sweeps from 130 to 200 °C at 150 °C for the example of the PS compound with 5 wt % O-BA/O-TP.

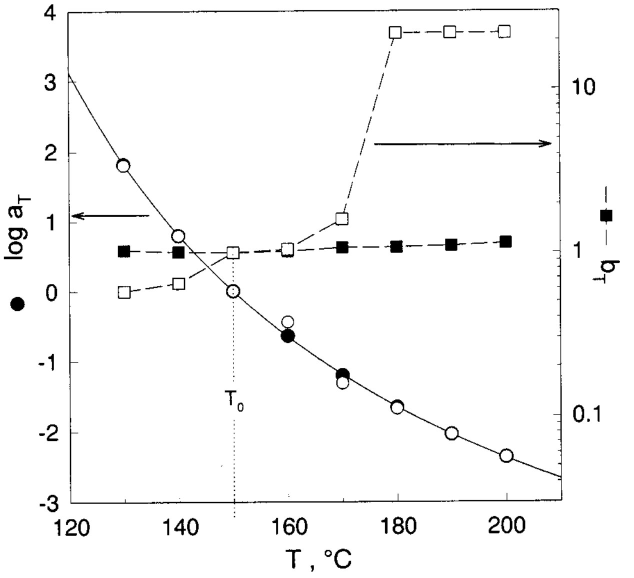

Figure 10. Horizontal (circles) and vertical (squares) shift factors, a_T and b_T, of the pure PS matrix (filled symbols) and the compound with 5 wt % O-BA/O-TP (open symbols).

As can be seen from Figure 9, the superposition of G' is fairly well in the plateau region, and also the shift of the three isotherms from 180 to 200 °C results in a smooth master curve for G' and G'' in the flow region with the typical slopes 2 and 1, respectively. The main deviations appear in G'' at high frequencies and in the low-frequency range for the temperatures from 130 to 170 °C. In the latter range, both G' and G'' split into two branches. In this region G'' shows a nearly constant slope of 0.4 (see line in Figure 9). The split into different branches can be accounted for by the reinforcing assembly structures, which melt above the critical temperature of about 179 °C. Up to now we have no conclusive explanation for the deviations in G'' at high frequencies. However, it seems to be a characteristic feature of these materials with a systematic temperature dependence.

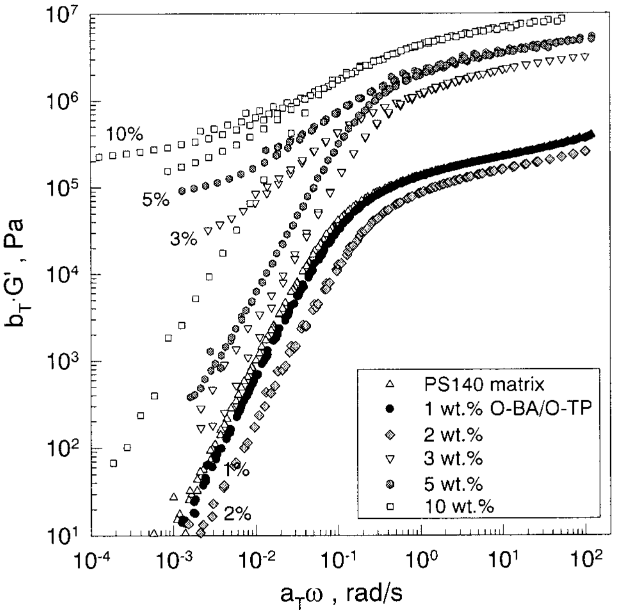

Figure 11. Superpositions of the storage modulus at 150 °C of the PS compounds with 0, 1, 2, 3, 5, and 10 wt % O-BA/O-TP.

Accounting for experimental errors and uncertainties in the shift procedure, the horizontal shift factors a_T of the matrix (filled points in Figure 10) and of the compounds (open circles) are indistinguishable. Thus, the temperature dependence of the viscosity in both cases follows WLF (Williams, Landel, Ferry) behavior. As already mentioned in context with the DSC measurements, this indicates that the viscoelastic softening behavior is dominated by the matrix over the complete covered temperature range. However, the vertical shift factors b_T of the pure matrix and the supramolecular structured sample strongly differ. The three highest isotherms have to be multiplied with b_T values of 22 to match the low-temperature isotherms. The drastic change in the vertical shift factors between 170 and 180 °C corresponds to the transition visible in the DSC measurements and the temperature cycles.

After the investigation of the external requirements for the structure formation in the compounds, we will focus in the following on an “internal condition”, the required concentration of the complementary tectons.

In Figure 11 superpositions of G' for six different concentrations of O-BA/O-TP in PS are compared at 150 °C. The single isotherms were shifted manually upon the reference temperature according to the procedure applied to the 5 wt % compound shown in Figure 9. Obviously, for low concentrations from 0 to 2 wt % the principle of time−temperature superposition is valid, and true master curves with the typical shape of linear, amorphous polymers are obtained. The master curve corresponding to the concentration of 1 wt % nearly matches the pure matrix and reveals the same plateau modulus and a viscosity only slightly lowered. For the sample with 2 wt % the shift to lower moduli and higher frequencies is more pronounced. Thus, addition of the O-BA/O-TP assembly only exerts a plastisizing effect in the matrix which increases with concentration. For amounts of 3 wt % and above, however, the shape of the curves and the direction of the concentration dependent shift change completely. Smooth master curves are no longer obtained, but G' and G'' split into two branches as already described. With increasing concen-

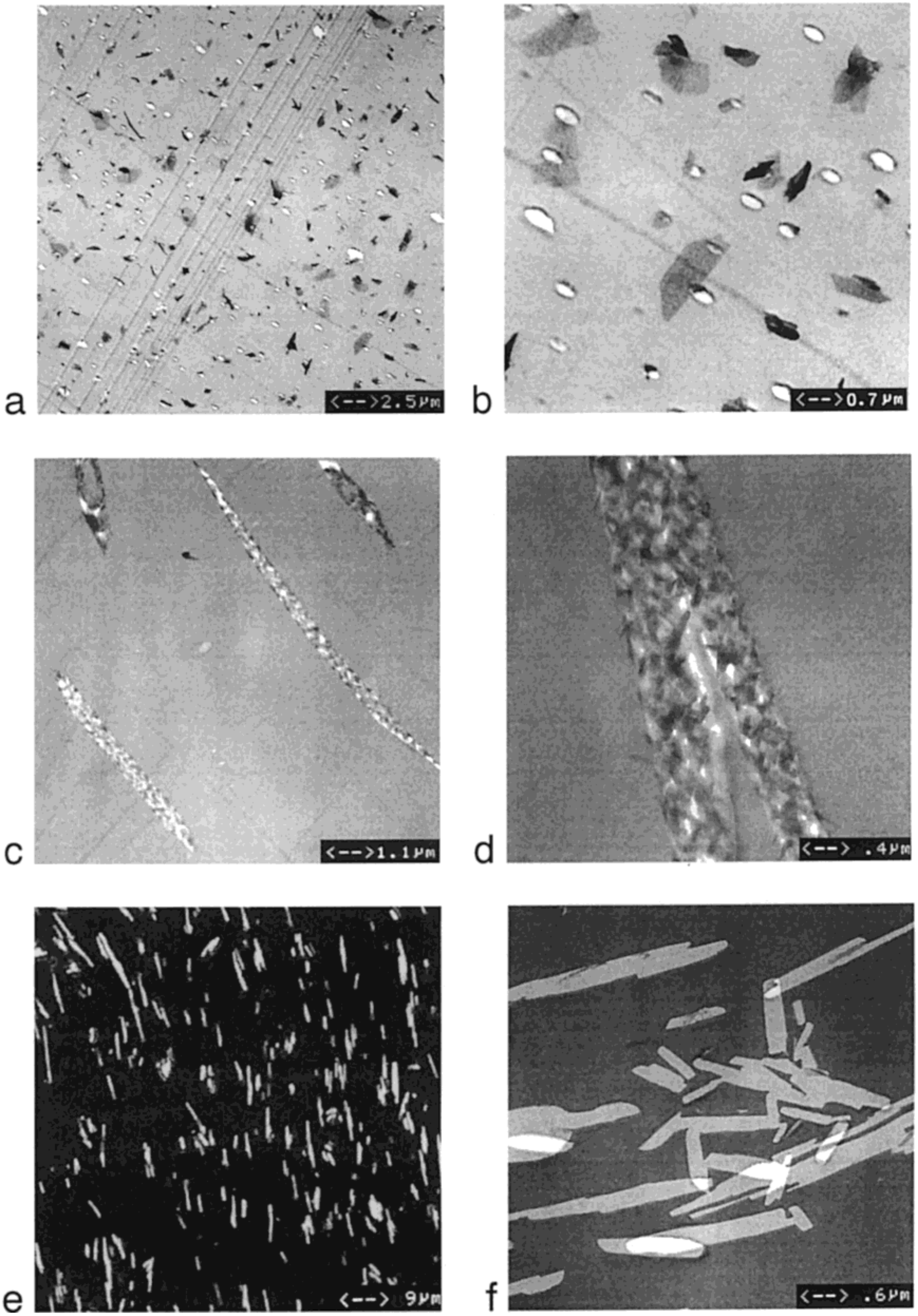

Figure 12. TEM micrographs of PS compounds: (a, b) O-BA/O-TP in PS prepared by melt extrusion; (c, d) the same compound after melt rheological treatment; (e, f) Bz-BA/Bz-TP in PS prepared by melt extrusion. All samples contain 10 wt % of assemblies.

tration of the tectons the curves now shift to higher moduli. The isotherms below 180 °C reveal the onset of a second plateau, typically observed for a network. From the increasing moduli in this low-frequency range it can be qualitatively deduced that the number of cross-links increases and the mesh size of the networklike structure decreases with tecton concentration. Further, a closer inspection of the low-frequency end shows that G' of the different isotherms does not superimpose perfectly but slightly decreases with increasing temperature. Thus, the reinforcing structures are not static but dynamic and slowly dissolve with increasing temperature until they break down completely above 180 °C.

D. Transmission Electron Microscopy. Compared with scattering techniques, transmission electron microscopy (TEM) renders the most versatile information

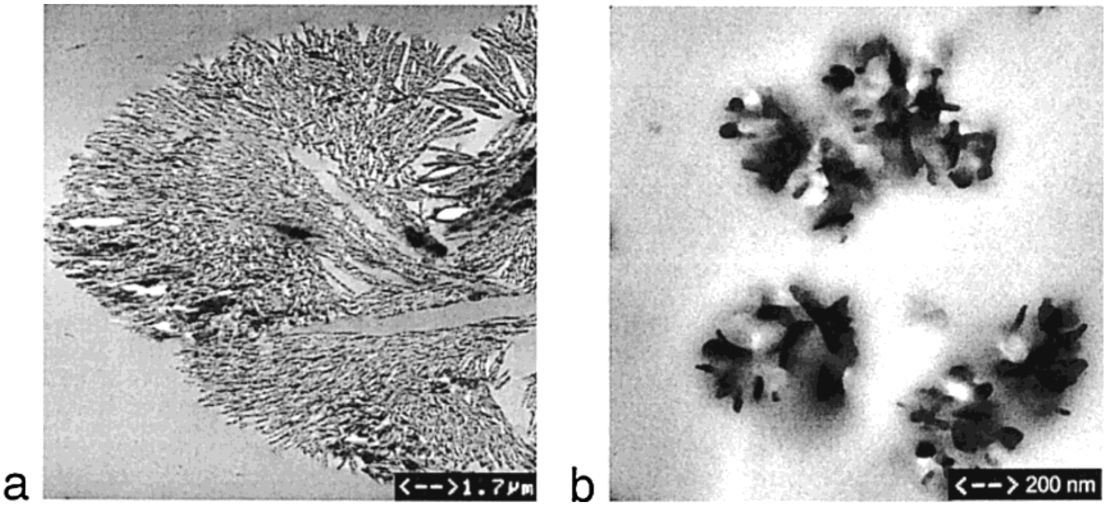

Figure 13. TEM micrographs of supramolecular assemblies in PMMA: (a) spherolites of O-BA/O-TP in polymerized MMA/PMMA mixture without melt extrusion; (b) Bz-BA/Bz-TP in PMMA prepared by melt extrusion. Both samples contain 10 wt % of assemblies.

about the size and shape of the assembly particles as well as about their three-dimensional arrangement on a submicron scale. The morphology of PS and PMMA specimens containing O-BA/O-TP and Bz-BA/Bz-TP has been investigated that way.

Figure 12a–f shows TEM micrographs of tectonic self-assemblies in PS containing 10 wt % of assemblies. The morphology observed depends on the substitution type of the tectons, as well as on the processing history. Figure 12a depicts the morphology of an extruded sample containing a 1:1 mixture of the octyl-substituted tectons in the PS matrix. O-BA/O-TP forms homogeneously distributed particles with a size ranging from 50 nm to 1 μm. The shape of these particles indicates the formation of layered crystals[11] (Figure 12b). Preparation of the samples by microtoming can cause the formation of holes, i.e., negative images of the particles, which then appear bright in the TEM micrographs.

Sections of samples after the rheological measurements in the temperature range between 140 and 200 °C reveal nearly quantitative agglomeration of the O-BA/O-TP particles as shown in Figure 12c,d. Inside of these extended agglomerates the nanoscaled particles are still visible. Therefore, it is deduced that these particles were nucleated independently and that the oscillatory shear deformation with small amplitudes then contributes to the formation of the agglomerates. In addition to the temperature dependence of the reversible self-assembling, this agglomeration process also accounts for the violation of the time–temperature superposition principle during the rheological measurements.

Figure 12e,f shows the typical appearance of the Bz-BA/Bz-TP assembly in the PS matrix. Similar to the octyl-substituted tectons, independently growing particles with a characteristic crystalline shape are formed. The main difference to the O-BA/O-TP compound is the much larger size of the particles ranging from 500 nm to several microns. In contrast to O-BA/O-TP, this morphology does not change during the rheological measurements. Because of the fact that neither morphology changes nor other physical transitions occur during the rheological measurements with the covered temperature range, it is expected that the principle of time–temperature superposition is valid. In fact, master curves have been successfully obtained.

Figure 13a shows the appearance of O-BA/O-TP (10 wt %) in a PMMA matrix. The sample has been prepared by dissolving the two tectons individually in MMA/PMMA. Pouring these solutions together leads to the crystallization of the O-BA/O-TP assembly. Subsequent polymerization of the mixtures at 60 °C produces large O-BA/O-TP spherulites with a central nucleus. The spherulitic shape is the result of branching and epitaxial ongrowth of O-BA/O-TP fibrils. Obviously, the number of nuclei formed in PMMA is very low. This effect becomes even more dramatic for melt extruded compounds. In this case crystalline superstructures are completely absent, and the presence of the polymer matrix totally suppresses the formation of the O-BA/O-TP assembly structures. This has been attributed to the polar chemical nature of PMMA disabling the formation of tectonic nuclei by hydrogen bonding. Therefore, no crystalline assembly particles can be found in extruded PMMA, in contrast to the numerous nanosized particles in PS.

Figure 13b depicts the supramolecular assembly of Bz-BA/Bz-TP in PMMA prepared by melt extrusion. In contrast to the O-BA/O-TP mixture in PMMA, Bz-BA/Bz-TP is able to form a crystalline assembly structure. Similar to O-BA/O-TP prepared without melt extrusion, flowerlike structures are formed. The size of these structures is much smaller than the size of the O-BA/O-TP spherulites, but nevertheless the growth also starts at central nuclei.

In summary, it can be stated that the tectons form independently growing crystals in a PS matrix, whereas in a PMMA matrix supramolecular structures evolve from a central nucleus, if structure formation is observed at all.

Conclusions

Already small amounts of complementary tectons such as the presented derivatives of barbituric acid (BA) and 2,4,6-triaminopyrimidine (TP) have the potential to form nanoscale superstructures in polymer matrices. These tectons readily melt in the matrix and self-organize even in highly viscous polymers via hydrogen bonding to produce supramolecular assemblies with significantly higher melting temperatures. We have investigated the prerequisites and the effects of the structure formation by dynamic-mechanical spectroscopy and transmission electron microscopy. Two different substitution patterns of the complementary tectons, i.e., octyl- and benzyl-substituted BA and TP, were used in the two different amorphous polymer matrices, polystyrene (PS) and poly(methyl methacrylate) (PMMA).

From the possible combinations, only the supramolecular self-assembly of O-BA and O-TP in PS leads to an outstanding change in the rheological behavior of the matrix. These compounds exhibit a networklike character with drastically increased dynamic moduli. The reinforcing impact of the assembly reverses to a plastisizing effect above 179 °C, which corresponds to the melting point of the neat assembly. PS compounds with benzyl-substituted tectons exhibit no comparable rheological effects, since large assembly particles once formed cannot reorganize due to the higher Bz-BA/Bz-TP melting point. We therefore conclude that superstructure formation is most efficient if the assembly self-organizes from a homogeneously dissolved state. This is of importance for the optimization of processing conditions but might also play a role for the nucleating effect of related compounds.

In melt extruded compounds with PMMA matrix, none of both complementary tectonic pairs form superstructures with remarkable rheological effects. Over the whole investigated temperature range the tectons exert a plastisizing effect on the polymer matrix. These findings indicate that the individual tectons or at best small assembly fragments are homogeneously distributed in the PMMA matrix and that the tectons efficiently interact separately with the polar matrix, e.g., by hydrogen bonding. It can be concluded that a certain degree of incompatibility between the tectons and the matrix is one prerequisite for the formation of superstructures. The quantitative evaluation of the different interactions, however, is difficult and must remain a future task.

Certain limitations for the structure formation exist with respect to the concentration of the tectons, the temperature, and the applied mechanical stress. In the case of the PS compounds with octyl-substituted tectons, network behavior is only found at concentrations of 3 wt % and above. Increasing the temperature beyond the melting point of the neat assembly as well as higher shear stresses leads to reversible breakdown of the reinforcing superstructures.

Future perspectives of the presented self-organizing systems comprise polymers with enhanced heat distortion temperatures at preserved thermoplastic processability and applications such as thixotropic or nucleating agents.

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