Molecular Tectonics. Disruption of Self-Association in Melts Derived from Hydrogen-Bonded Solids

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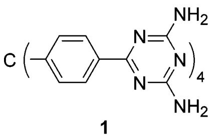
ABSTRACT: An effective strategy for making new ordered molecular materials by design is to build them from subunits that associate with their neighbors and thereby hold them in predetermined positions. Such tectons can be made by attaching multiple peripheral sites of association to geometrically suitable cores. In tectons **3**−**5**, for example, simple triaminotriazine groups grafted to a nominally tetrahedral tetraphenylmethyl core form intermolecular hydrogen bonds according to reliable motifs, and crystallization thereby leads to the formation of porous three-dimensional networks. Functionalization of the triaminotriazine groups with alkyl chains gives rise to amorphous tectons, and the increase of the chain length lowers the glass transition temperatures of these materials, allowing their association in the melt to be studied by rheological methods. The rheological properties depend in a characteristic way on the length of the alkyl substituents. In particular, viscosity and T_g both decrease with increasing length of the alkyl chains in the series of tectons **7**−**10**, suggesting that intertectonic hydrogen bonding is increasingly diminished by the steric effects of the substituents. In this way, formation of extended hydrogen-bonded networks becomes gradually unfavorable, and mobility and fluidity are enhanced. For these reasons, melts derived from tectons **7**−**10** do not behave like conventional linear polymers or dendrimers, but rather form a novel class of materials with unique properties of their own.

Introduction

Molecules that associate predictably with multiple neighbors are valuable components for the construction of new materials because they allow for controlling to a certain degree the supramolecular architectures. Such molecules have been called *tectons* from the Greek word for builder.[2] Typically, they incorporate multiple peripheral sticky sites that direct association according to well-established motifs, linked to a core that holds the sticky sites in suitable orientations. The strategy of using such subunits for the programmed construction of materials, which has been called molecular tectonics,[2,3] has begun to have a particularly important impact in the field of crystal engineering.[4,5] For example, crystallization of tecton **1** is directed by hydrogen bonding of aminotriazine groups according to motif **2**, leading ultimately to the formation of a robust three-dimensional network in which each tecton is linked to eight neighbors by a total of 16 hydrogen bonds.[6] Similar three-dimensional hydrogen-bonded networks are also generated by crystallizing analogue **3** and its substituted derivatives **4** and **5**.[7,8]

Such networks can be considered to be solid supramolecular polymers in which monomeric tectons of low molecular weight are linked by numerous strong noncovalent interactions, rather than by covalent bonds as in conventional polymers.[9−12] Supramolecular nanotubes, liquid crystalline materials, and nanostructured gels formed in aqueous and organic media[10] have been obtained and characterized.



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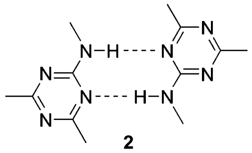

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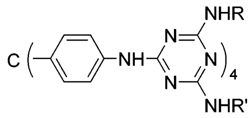

3 (R = R' = H)
4 (R = R' = $CH_2CH{=}CH_2$)
5 (R = $CH_2CH_2OCOCH_3$, R' = H)
6 (R = R' = $(CH_2)_3CH_3$)
7 (R = R' = $(CH_2)_5CH_3$)
8 (R = R' = $(CH_2)_7CH_3$)
9 (R = R' = $(CH_2)_9CH_3$)
10 (R = R' = $(CH_2)_{11}CH_3$)

Fuchs et al.,[13] having built nanostructures via association of tectons in several polymer matrices, obtained homogeneous mixtures exhibiting significant changes in the thermal and physical properties from that of the original matrices. Liquid crystalline phases were also observed when using hydrogen-bonded association of polymers chain in melts.[14] Supramolecular polymers formed from telechelic siloxanes as reported by Hirschberg et al.[15] show association via quadruple hydrogen bonds due to the presence of ureido-pyrimidone functional groups.

The same ureido-pyrimidinone groups were used by Meijer et al.[16] for the formation of reversible polymer networks using self-complementary. Those supramolecular networks exhibit a viscoelastic behavior, which responds to temperature and concentration changes. They have shown that while the solution

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viscosity of such compounds was easily characterized, it was difficult to obtain their bulk rheological characteristics because of their strong tendency to crystallize. Consequently, data were reported on systems containing siloxane spacers, which exhibit a polymer-like viscoelastic behavior. The reversible network obtained when combining trifunctionals copolymers of propylene oxide and ethylene oxide and methylcytosine showed also some interesting rheological features. The reversible cross-links behaved like entanglements in a linear polymer.

Many other authors such as Lehn, Reinhoudt, Whitesides, Wuest, and Zimmerman have made particularly significant contributions to the development of this exciting area of chemistry,[16,17] which has been the subject of multiple reviews.[18] If modifying the end groups functionality for tuning the physical properties of such materials is a useful strategy, other approaches may be used. In related work, Friedrich, Mülhaupt, and others have added small amounts of network-forming tectons to modify the rheological properties of conventional covalent polymers.[19] Similarly, Coates, Fréchet, Long, Rotello, Stadler, and others have examined the effect of intentionally introducing hydrogen-bonding groups at various positions along the main chains of conventional covalent polymers.[20] Interchain hydrogen bonding in such modified polymers creates thermoreversible networks, thereby providing an effective approach for altering rheological properties as a function of the number of hydrogen-bonding sites introduced. As illustrated by the work of Fréchet, Griffin, and others, hydrogen-bonded supramolecular polymers of various types are promising candidates for the formation of liquid crystals, gels, and other new ordered materials.[14,21]

So far, molecular tectonics has been used most notably to engineer crystalline solids, but the strategy also promises to help regulate association in other condensed media such as gels, mesophases, amorphous polymers, and even liquids. Unfortunately, typical tectons such as compounds **1**, **3**, **4**, **5**, and **6** have high melting points, so their aggregation in the melt cannot be studied conveniently. To decrease melting points, we prepared the series of octaalkyl derivatives **7**−**10**. Close structural similarity to simple models **3**−**6** ensured that tectons **7**−**10** would also form three-dimensional hydrogen-bonded networks in the solid state, yet might melt at relatively low temperatures to give partially ordered fluids in which extensive hydrogen bonding is maintained. Like other supramolecular polymers joined thermoreversibly by weak interactions, such melts would be expected to exhibit highly temperature-dependent viscoelastic behavior. The expected pseudopolymer should behave as a reversible network when scanning through the melt transition. Farrington et al.[22] have presented a similar concept in the study of the melt viscosity of dendritic macromolecules. They observed that the viscosity is much more temperature dependent for an end group substituted dendrimer. Furthermore, those end groups have a larger effect on the melt viscosity compared to the effects induced by the substitution on the core of the dendrimer. In this paper, we show that the rheological properties of amorphous tectons **7**−**10** in the melt depend in a characteristic way on the length of the alkyl substituents. We have performed structural characterization by polarized light microscopy and X-ray powder diffraction showing that these systems are amorphous. Micrographs are provided in the Supporting Information.

Experimental Section

Synthesis of Tetrakis[4-[[4,6-bis(hexylamino)-1,3,5-triazin-2-yl]amino]phenyl]methane (7). A solution of tetrakis[4-[(2,4-dichloro-1,3,5-triazin-6-yl)amino]phenyl]methane (7.40 g, 7.61 mmol)[7,8] in tetrahydrofuran (THF; 60 mL) was stirred at 25 °C and treated with pentylamine (18 mL). The resulting mixture was heated at reflux for 4 h. Volatiles were then removed by evaporation under reduced pressure, a 1:1 mixture (150 mL) of CH_3OH and water was added, and the resulting suspension was stirred for 1 h. The precipitate was separated by filtration, rinsed with CH_3OH, and triturated with acetone. Filtration then yielded tetrakis[4-[[4,6-bis(hexylamino)-1,3,5-triazin-2-yl]amino]phenyl]methane (**7**; 11.1 g, 7.45 mmol, 98%) as an analytically pure colorless solid; mp 140−155 °C (softening, broad transition). IR (KBr): 3431, 3273, 2954, 2927, 2855, 1571, 1507, 1416, 1358, 1233, 1187, 810 cm $^{-1}$. ^{1}H NMR (400 MHz, DMSO-d_6, 100 °C):[15] δ 8.08 (s, 4H), 7.64 (d, $^3J = 8.8$ Hz, 8H), 7.02 (d, $^3J = 8.8$ Hz, 8H), 6.02 (s, 8H), 3.28 (m, 16H), 1.54 (m, 16H), 1.31 (m, 48H), 0.86 (t, $^3J = 6.8$ Hz, 24H). ^{13}C NMR (100 MHz, DMSO-d_6, 100 °C):[15] δ 165.5, 163.7, 139.5, 137.8, 129.7, 117.7, 61.9, 39.6, 30.3, 28.7, 25.4, 21.2, 12.8. MS (FAB, 3-nitrobenzyl alcohol) *m/e* 1490. Anal. Calcd for $C_{85}H_{132}N_{24}$: C, 68.51; H, 8.93; N, 22.56. Found: C, 68.15; H, 9.19; N, 22.44.

Synthesis of Tetrakis[4-[[4,6-bis(octylamino)-1,3,5-triazin-2-yl]amino]phenyl]methane (8). An analogous reaction was carried out with octylamine. After the mixture had been heated at reflux and volatiles had been removed by evaporation under reduced pressure, the residue was extracted with $CHCl_3$. The extracts were washed with aqueous HCl (3 N), aqueous NaOH (1 N), and then with water until the washings were neutral. The washed extracts were dried over anhydrous Na_2SO_4, and removal of solvent by evaporation under reduced pressure then yielded tetrakis[4-[[4,6-bis(octylamino)-1,3,5-triazin-2-yl]amino]phenyl]methane (**7**) in 89% yield as an analytically pure colorless solid; mp 130−133 °C (softening, broad transition). IR (KBr): 3442, 3270, 2928, 2856, 1573, 1507, 1419, 1359, 1215, 810 cm $^{-1}$. ^{1}H NMR (300 MHz, DMSO-d_6, 100 °C):[15] δ 8.29 (s, 4H), 7.65 (d, $^3J = 8.9$ Hz, 8H), 6.98 (d, $^3J = 8.9$ Hz, 8H), 6.21 (m, 8H), 3.25 (m, 16H), 1.52 (m, 16H), 1.27 (m, 80H), 0.84 (t, $^3J = 6.7$ Hz, 24H). ^{13}C NMR (75 MHz, DMSO-d_6, 100 °C):[15] δ 165.6, 163.8, 139.6, 138.0, 129.9, 117.8, 61.5, 39.2, 30.7, 29.0, 28.3, 28.1, 26.0, 21.4, 13.1. MS (MALDI TOF) *m/e* 1713. Anal. Calcd for $C_{101}H_{164}N_{24}$: C, 70.75; H, 9.64; N, 19.61. Found: C, 70.90; H, 10.21; N, 19.54.

Synthesis of Tetrakis[4-[[4,6-bis(decylamino)-1,3,5-triazin-2-yl]amino]phenyl]methane (9). An analogous procedure with decylamine gave tetrakis[4-[[4,6-bis(decylamino)-1,3,5-triazin-2-yl]amino]phenyl]methane (**9**) in 80% yield as an analytically pure colorless solid; mp 115−128 °C (softening, broad transition). IR (KBr): 3431, 3404, 3269, 3168, 2954, 2923, 2853, 1574, 1503, 1415, 1355, 1234, 1186, 810 cm $^{-1}$. ^{1}H NMR (400 MHz, DMSO-d_6, 100 °C):[15] δ 8.23 (s, 4H), 7.65 (d, $^3J = 8.9$ Hz, 8H), 6.99 (d, $^3J = 8.9$ Hz, 8H), 6.16 (m, 8H), 3.25 (m, 16H), 1.52 (m, 16H), 1.24 (m, 112H), 0.84 (t, $^3J = 6.7$ Hz, 24H). ^{13}C NMR (100 MHz, DMSO-d_6, 100 °C):[23] δ 165.5, 163.7, 139.5, 137.8, 129.7, 117.7, 61.9, 39.6, 30.6, 28.8, 28.3, 28.2, 28.2, 27.9, 25.9, 21.3, 13.0. MS (MALDI TOF) *m/e* 1937. Anal. Calcd for $C_{117}H_{196}N_{24}$: C, 72.47; H, 10.19; N, 17.34. Found: C, 72.35; H, 10.25; N, 17.36.

Synthesis of Tetrakis[4-[[4,6-bis(dodecylamino)-1,3,5-triazin-2-yl]amino]phenyl]methane (10). Analogous reactions with dodecylamine gave compound **10** in similarly high yields as analytically pure colorless solids.

Thermal Analysis. Modulated differential scanning calorimetry (MDSC)[24a] was carried out with a TA Instruments Q1000 calorimeter, using a 60 s period and a heating rate of 2 °C/min from 10 to 200 °C. The results reported were recorded after an initial cycle of melting and resolidification.

Melt Rheology. A Rheometric Scientific SR5000 controlled stress rheometer was employed to measure the dependence

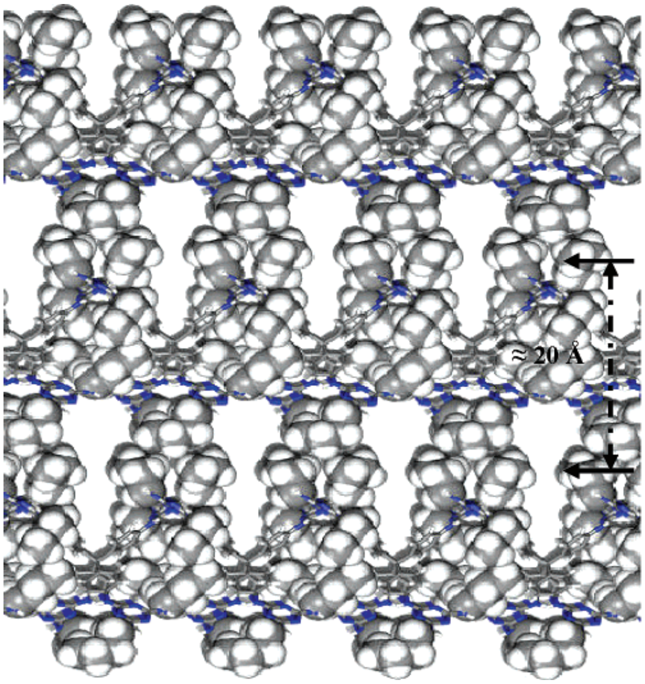

Figure 1. View of the structure of tetrakis[4-[[4,6-bis(bis(butylamino)-1,3,5-triazin-2-yl]amino]phenyl]methane along the *b* axis showing a 4 × 2 × 2 array of units cells.

of rheological properties on temperature in steady-state and dynamic modes. The dependence of the rheological parameters on temperature was examined over a range extending from 50 to 160 °C, using a heating/cooling rate of 3 °C/min. For all the temperature dependence experiments, parallel plates with a diameter of 25 mm were used. The steady-shear behavior at high temperatures was analyzed using a cone/plate configuration with a 40 mm diameter and a 2° angle cone. The gap between the plates was set at 2 mm in the parallel plate configuration and at 52 μm in the cone/plate configuration. Steady-shear measurements were performed in a controlled-stress mode over a range of shear stresses from 0.07 to 10 000 Pa, corresponding to nearly 6 decades of the shear range from 0.0001 to 100 s^{-1}. Dynamic rheological measurements were performed between 0.01 and 100 Hz at constant stress. The constant stress conditions were determined by dynamic stress sweeps across the range of frequencies used. NMR spectroscopy and thermogravimetric analyses ensured that tectons **7**−**10** remained stable under the conditions of elevated temperature reached in the course of melt rheology experiments, and none of the compounds showed any signs of decomposition below 200 °C. In addition, repeated measurements of the melt viscosity of selected samples were reproducible, and the values observed varied by less than 1%.

Results and Discussion

Structural Characterization. X-ray diffraction powder diagrams were performed on tectons **7**−**10** to check the crystallinity of the crude products. All the tectons display the same kind of diffraction pattern (Figure 1) with a broad peak between 20° and 30° in 2θ that is characteristics of amorphous systems and a narrow peak around 5° in 2θ. The position of this peak at low diffraction angle varies with the length of the alkyl chain and is compatible with an organization at a large scale. The compounds before recrystallization can be described as amorphous. We have been able to crystallize tectons **6** by slow evaporation of a solution of the amorphous product in dioxane. Crystals of suitable quality for an X-ray diffraction experiment were obtained and used to determine the crystal structure of tecton **6** in order to get some information on the structural properties of these systems. Tecton **6** crystallizes as an inclusion compound with dioxane to give a three-dimensional supramolecular network. In the structure, each molecule is linked with eight neighbors by hydrogen bonds involving the diaminotriazine units. Interestingly, this hydrogen bond association defines layers of molecules while weaker van der Waals interactions ensure the cohesion between the hydrogen-bonded layers. The resulting structure is porous, and 47% of the volume in the lattice remains available for including the dioxane guest molecules in interconnected channels. These channels are positioned in planes perpendicular to the *c* axis while no porosity is observed along the *c* axis. Remarkably, the butylamine chains are not confined between the sheets, but some of them are located within them. One can deduce from this arrangement that increasing the length of the alkyl chains will have some effect on the ability to keep all the hydrogen bonds between molecules. Because of the steric encumbrance induced by longer alkyl chains lying within the hydrogen-bonded layers, one can expect that the hydrogen bond association may be more difficult when increasing the alkyl chain length. Ultimately, longer chain will disrupt the hydrogen bond recognition, and such a trend in the crystalline state may be also extrapolated in the amorphous compounds that are the subject of the present investigation. More information about the crystal structure and the powder X-ray diffraction patterns are provided in the Supporting Information.

Table 1. T_g Data for Amorphous Tectons

tecton identification	no. of carbon atoms in alkyl chains	T_g (°C)[a]
7	6	135
8	8	122
9	10	115
10	12	113

[a] T_g values are measured at half-transition.

Thermal Properties. Tectons **7**−**10** melted over wide ranges of temperatures, and their behavior resembled the glass transitions of polymers. Table 1 lists the values of the glass transition temperatures (T_g) for the tectons vs their alkyl chain length. To evaluate accurately the values of T_g, we used modulated differential scanning calorimetry (MDSC),[24a] which enables the total heat flow to be separated into a component associated with heat capacity (reversing signal) and a kinetic component (nonreversing signal). Because of the importance of the enthalpic relaxation, all values of T_g were obtained from the reverse heat flow curve rather than from the total heat flow curve (Figure 2). MDSC experiments establish that tectons **7**−**10** behave more like conventional amorphous polymers than like crystalline substances, and they attain a rubbery state at T_g. Qualitative differences among the MDSC profiles can be noted. In particular, T_g for tectons **8** (with C_6, C_8,) is relatively sharp, whereas the profiles for tectons **9** and **10** (C_{10} and C_{12} chains) extend over a wider range of temperatures. A close examination of the signals does not indicate clearly the presence of a second transition after T_g.

Figure 3 shows how T_g depends on the number of carbon atoms (or tectons M_w) in the alkyl chains of tectons **7**−**10**. The values of T_g span a range of about 25 °C and decrease as the chain length increases according to a power law relationship. Several structural

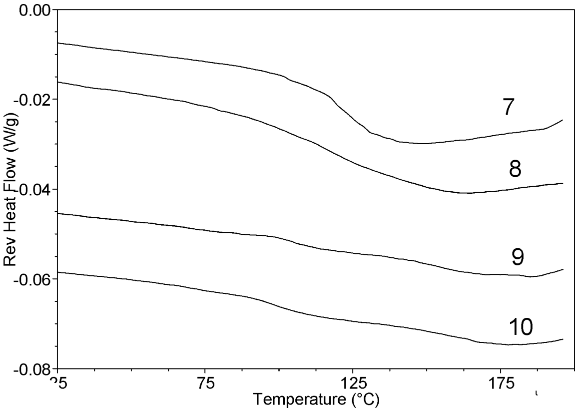

Figure 2. MDSC thermograms of tectons **7**−**10** (alkyl chains of C_6, C_8, C_{10}, and C_{12}, respectively).

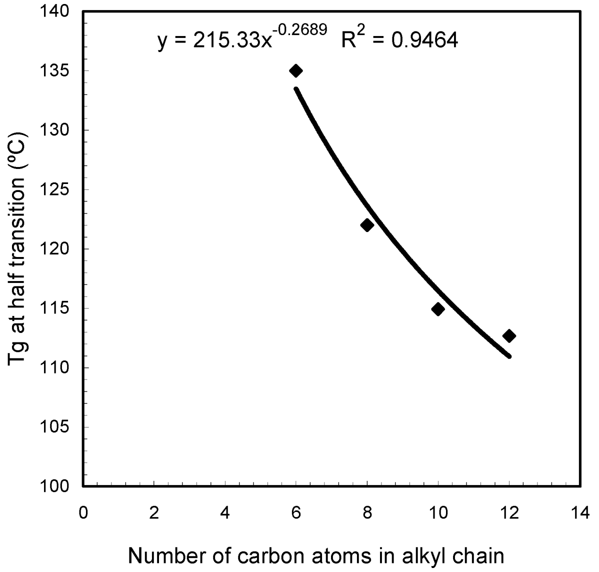

Figure 3. Dependence of T_g with the number of carbon atoms in the alkyl chains for tectons **7**−**10** (C_6, C_8, C_{10}, and C_{12}, respectively).

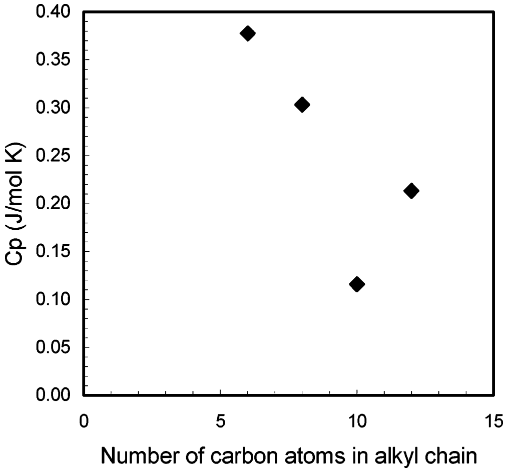

Figure 4. Dependence of C_p with the number of carbon atoms in the alkyl chains for tectons **7**−**10** (C_6, C_8, C_{10}, and C_{12}, respectively).

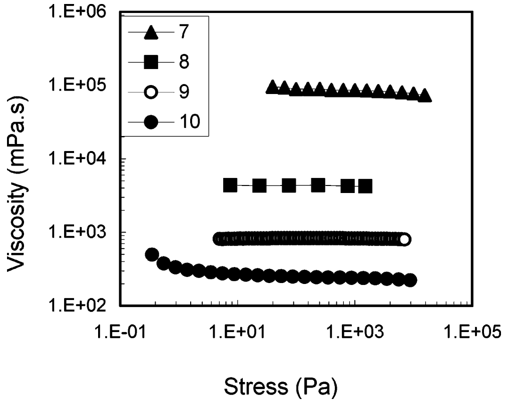

Figure 5. Steady-stress viscosity of tectons **7**−**10** (C_6, C_8, C_{10}, and C_{12}, respectively) as a function of stress at 140 °C.

and chemical factors can usually affect the glass transition temperature of polymers. One of these factors is the molecular weight, and for conventional amorphous polymers, such as polystyrene, the evolution of T_g with M_w follows classical power law relationships. In these systems, T_g increases with M_w, starting from oligomers to high M_w, with a separate dependence for each M_w region.[24b] It is of interest to note that, while the tectons have values of M_w in the thousand ranges, they exhibit T_g values equivalent to that of higher conventional amorphous polymers. Indeed, such polymers as polystyrene have T_g at around 100 °C for M_w greater than 30 000, whereas individual tectons exhibit similar high T_g values for molecular weight 10 times lower. Longer chains therefore appear to permit more molecular motion, even though they increase molecular weight. We interpret these observations as evidence that lengthening the alkyl chains interferes increasingly with intertectonic hydrogen bonding and thereby reduces hydrogen bonding association, possibly because of steric effects. It is expected that the increased fluidity of the tectonic system might favor some degree of entanglements as observed in classical polymeric systems. Another factor that may influence the value of the glass transition temperature is chain stiffness or flexibility of the polymer chains. Main chain aliphatic groups will build flexibility into a polymer and lower T_g; alkyl side chains will also lower T_g. It is well documented that the T_g of methacrylate polymers decreases with the length of the aliphatic groups from 65 °C for an ethyl group down to −65 °C for a *n*-dodecyl side chain.[24c] While the tectonic systems are becoming bulky, the introduction of aliphatic chains decreases the stiffness of the whole structure. The high values of T_g associated with low molecular weight can be interpreted as an indication of the existence of some degree of networking through interdigitation.

Figure 4 reveals that the heat capacity (C_p) associated with T_g decreases in tectons **7**−**10** as the chain length increases, with the conspicuous exception of compound **10** (C_{12}). The general tendency of C_p to decrease is consistent with the transformation of strongly associated and ordered solids into increasingly mobile fluids. As discussed further below, the unexpectedly high value of C_p in tecton **10** (C_{12}) can be attributed to restructuring of the alkyl chains induced by melting.

Melt Rheology (Steady Stress). Under steady-stress conditions, all tectons showed nearly constant viscous behavior at all applied stresses and temperatures investigated. This is illustrated by Figure 5, which presents data recorded at 140 °C. No experiments below 140 °C were conducted because of the high viscosity of tecton **7** (C_6) under these conditions. No evidence of association in the melt is visible in these data except at low values of stress, where the viscosity of tecton **10** (C_{12}) showed a slight dependence on shear, possibly

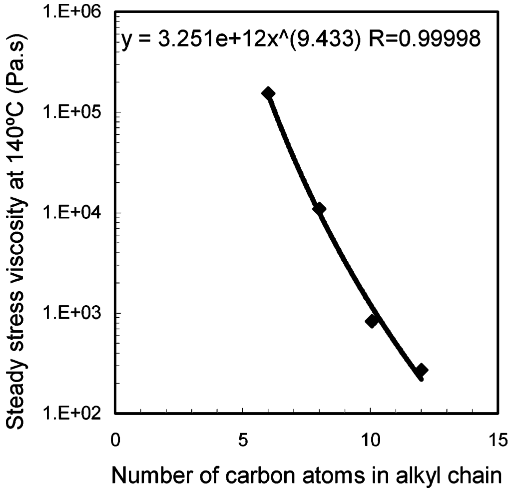

Figure 6. Dependence of steady-stress viscosity at 140 °C with the number of carbon atoms in the alkyl chains for tectons **7**−**10** (C_6, C_8, C_{10}, and C_{12}, respectively).

signaling a degree of structuring in the melt. Lengthening of the alkyl chains may favor less compact conformations with increasingly extended chains. If so, interdigitation may occur at temperatures above T_g, leading to structuring in the melt. Such a phenomenon could explain the small increase in the value of C_p observed for tecton **10** (C_{12}), even though T_g decreases.

Figure 6 shows how steady-stress viscosity depends on the length of the alkyl chains in tectons **7**−**10**. The relationship obeys a power law with a correlation coefficient close to unity ($R = 0.999$). It is instructive to compare the behavior of nominally tetrahedral tectons **7**−**10** with that of first-generation dendrimers of similar geometry.[25] In this comparison, the tetraphenylmethane core and attached triaminotriazine groups of tectons **7**−**10** can be taken together as a unit and considered equivalent to the core of an analogous dendrimer, while the alkyl groups of the tectons correspond to the branching arms of the dendrimer. In the case of dendrimers, viscosity *increases* with increasing molecular weight but does not follow the same type of relationship with molecular weight as observed in traditional linear polymers.[22,26] In the case of tectons **7**−**10**, a power law is also obeyed, but viscosity *decreases* with increasing molecular weight.

Decreasing values of viscosity and T_g with increasing length of the alkyl chains in tectons **7**−**10** are both consistent with reduced intertectonic hydrogen bonding caused by the increasingly large steric effects of the substituents. Formation of extended networks of hydrogen bonds is increasingly unfavorable, and mobility and fluidity are enhanced. As a result, melts derived from tectons **7**−**10** behave neither like dendrimers nor like conventional linear polymers, but rather form a novel class of materials with unique properties of their own.

Dynamic Analyses. The dynamic mechanical behavior of tectons **7**−**10** was examined at different temperatures and frequencies to assess the effect of the length of the alkyl chains on the degree of association in the melt. Figure 7 shows how the dynamic storage moduli (G') and loss moduli (G'') at 140 °C depend on frequency. Tectons **7**−**10** all behave essentially as fluids across the entire range of frequencies ($G' < G''$). whereas in tecton **6** G' and G'' cross each other at around a frequency of 2 Hz. However, two features of the dependence of the storage moduli (G') on frequency (Figure 7a) deserve further comment. One is that tecton **7** (C_6) appears to reach a rubbery plateau at high frequencies, possibly because the temperature of measurement (140 °C) is close to T_g. The second unanticipated feature is the higher G' value for tecton **9** (C_{10}) than that of tecton **10** (C_{12}) at frequencies below 1 Hz, which may be related to the hypothetical restructuring of compound **10** in the rubbery state, as discussed above.

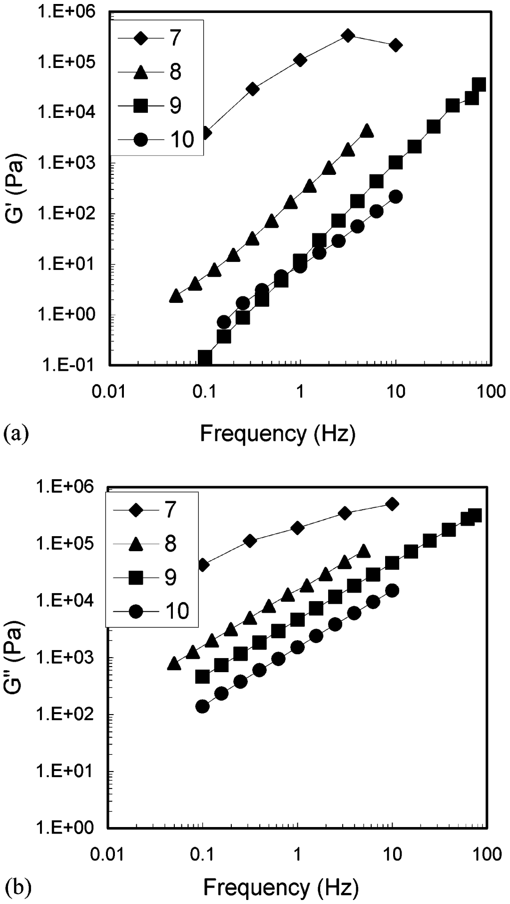

Figure 7. Dependence of storage moduli (G') (a) and loss moduli (G'') (b) with frequency at 140 °C for tectons **7**−**10** (alkyl chains of C_6, C_8, C_{10}, and C_{12}, respectively).

Tectons **7**−**10** all show essentially Newtonian behavior under steady stress (Figure 5), but they respond differently to dynamic shearing (Figure 8). The complex viscosities of tectons **8**, **9**, and **10** (with C_8, C_{10}, and C_{12} chains, respectively) are independent of frequency, which is characteristic of low molecular weight polymers' behavior below the entanglement molecular weight, but the viscosity of tecton **7** (C_6) showed a pronounced dependence. Although the shear thinning observed in the case of tecton **7** may result from association in the melt at rest, we believe that the behavior is more likely due to the proximity of T_g. A similar phenomenon has been noted in studies of the complex viscosity of dendrimers, which show generation-dependent shear thinning.[27] For this reason, tecton **7** (C_6) would be expected to exhibit more elastic behavior than tectons with longer alkyl chains.

Further information about tectons **7**−**10** was obtained by studying the dependence of their storage and loss moduli on temperature at a constant frequency of 1 Hz (Figure 9). In all cases, the moduli decrease monotonically once the glass transition is reached, as it would

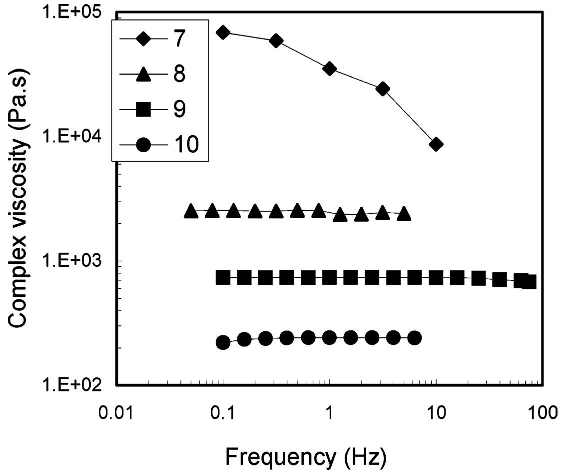

Figure 8. Dependence of complex viscosity with frequency at 140 °C for tectons **7**−**10** (C_6, C_8, C_{10}, and C_{12}, respectively).

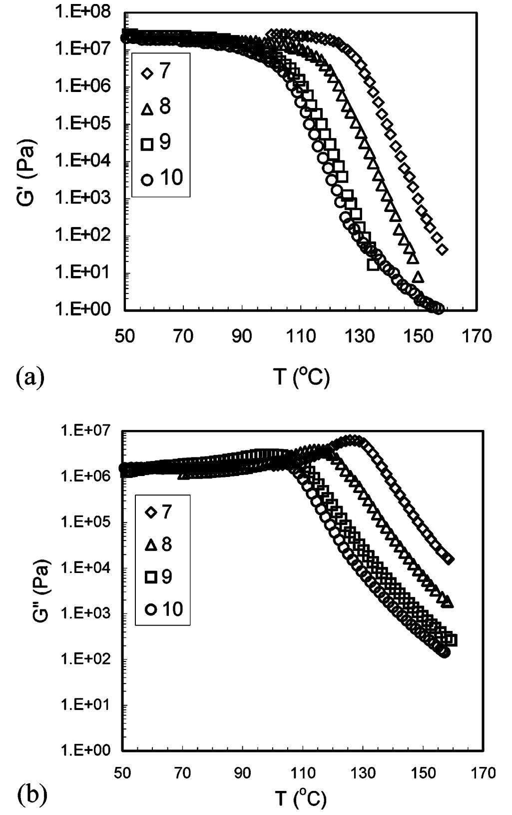

Figure 9. Dependence of storage moduli (*G*′) (a) and loss moduli (*G*″) (b) on temperature at 1 Hz for tectons **7**−**10** (alkyl chains of C_6, C_8, C_{10}, and C_{12}, respectively).

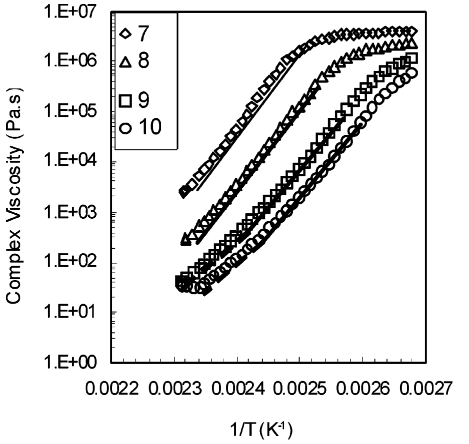

Figure 10. Semilogarithmic plot of the complex melt viscosity at 1 Hz against the reciprocal of the absolute temperature of tectons **7**−**10** (C_6, C_8, C_{10}, and C_{12}, respectively).

be expected for an amorphous system. Moreover, the moduli typically decrease as the length of the alkyl chains increases, reflecting the increased fluidity of the systems. However, two special features of Figure 9a warrant further discussion. The data for tectons **9** and **10** (C_{10} and C_{12}, respectively) suggest that the decreasing storage moduli may reach a plateau, at least for longer alkyl chains. The tectons **7**, **8**, and **9** do not exhibit any more elastic behavior at temperatures greater than 30 °C above their T_g while the storage modulus of tecton **10** does not continue to decrease monotonically as the temperature rises above 125 °C, possibly because the alkyl chains have become mobile enough to allow the number of intermolecular hydrogen bonds to increase, to cause greater entanglement, or to favor interdigitation of the chains.

The increased elastic response of tecton **10** should be reflected in the activation parameters for stress relaxation derived from the temperature dependence of the zero-shear viscosity. For tecton **6**, the viscosity at low frequency was taken equivalent to the zero-shear viscosity. The melt flow activation energy activation is obtained by calculating the activation parameters for tectons **7**−**10** determined from the temperature dependence of the complex viscosity (Figure 10) according to eq 1

$$\eta = A\mathrm{e}^{\Delta H/RT} \tag{1}$$

where η is the viscosity (Pa s), A is a constant, ΔH is the flow activation energy (J/mol), R is the gas constant (J mol K), and T is the temperature (K). For tectons **9** and **10** (C_{10} and C_{12}, respectively), the slope was measured over the range of temperatures extending from T_g to 130 °C. At higher temperatures, changes of slope are clearly visible, whereas for tectons **7** and **8** (C_6 and C_8, respectively), the slope was essentially unchanged between T_g and the highest temperature examined (approximately 160 °C). In the principal ranges of temperature, the activation parameters measured for tectons **7**−**10** all have values close to 300 kJ/mol, indicating a rapid transition from solid to fluid states. For longer-chain tectons **9** and **10**, the value drops to 190−220 kJ/mol above 130 °C. The effect is particularly marked in the plot for tecton **10** (C_{12}), which is consistent with an increase in intermolecular hydrogen bonding, entanglement, or interdigitation.

Conclusion

An effective strategy for making new ordered molecular materials by design is to build them from subunits that associate with their neighbors and thereby hold them in predetermined positions. Such subunits can be made by attaching multiple peripheral sites of association to geometrically suitable cores. In tectons **3**−**5**, for example, simple triaminotriazine groups grafted to a nominally tetrahedral tetraphenylmethyl core form intermolecular hydrogen bonds according to reliable motifs, and crystallization thereby leads to the formation of porous three-dimensional networks. Functionalization of the triaminotriazine groups with increasingly long alkyl chains lowers the glass transition temperatures of these materials and allows their association in the melt to be studied by rheological methods. The rheological properties depend in a characteristic way on the length of the alkyl substituents. In particular, viscosity and T_g both decrease with increasing length of the alkyl chains in the series of tectons **7**−**10**, suggesting that intertectonic hydrogen bonding is increasingly diminished by the steric effects of the substituents. In this way, formation of extended hydrogen-bonded networks becomes increasingly unfavorable, and mobility and fluidity are enhanced. For these reasons, melts derived from tectons **7**−**10** do not behave like conventional linear polymers or dendrimers, but rather form a novel class of materials with unique properties of their own. We believe that such substances, either as pure compounds or in mixtures, can be used to make valuable new materials with viscosities that vary significantly in response to conditions, such as changes in temperature.

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Supporting Information Available: Polarized light microscopy experiments; figure showing bright field micrographs. This material is available free of charge via the Internet at http://pubs.acs.org.

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