THE JOURNAL OF
PHYSICAL CHEMISTRY B

ARTICLE

pubs.acs.org/JPCB

Molecular Engineering of the Glass Transition: Glass-Forming Ability across a Homologous Series of Cyclic Stilbenes

Wen Ping

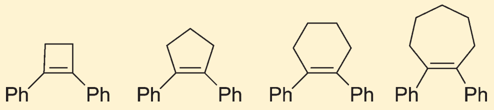
Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China

Daniel Paraska, Robert Baker, and Peter Harrowell*

School of Chemistry, University of Sydney, NSW 2006, Sydney, Australia

C. Austen Angell

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona, United States



ABSTRACT: We report on the glass-forming abilities of the homologous series 1,2-diphenylcyclo-butene, pentene, hexene and heptene—a series that retains the *cis*-phenyl configuration characteristic of the well-studied glass former, *o*-terphenyl. We find that the glass-forming ability shows a sharp maximum for the six-membered ring and demonstrate that this trend in glass-forming ability is a consequence of a maximum, for the 1, 2-diphenylcyclohexene, of the reduced glass transition temperature T_g/T_m. Since the nonmonotonic trend in T_g/T_m is entirely due to variations in T_m, we conclude that the design target for maximizing the glass-forming ability across an homologous series should focus on the crystal stability and the factors that determine it.

1. INTRODUCTION

o-Terphenyl (OTP) is an example of a small nonpolar molecule that is a good glass former.[1] This means that OTP exhibits a reversible transition between glass and liquid under moderate rates of temperature change and, as a result, has been used extensively in studies of the glass transition. Despite this attention, we do not know why OTP is a good glass former. In general, we know very little about what aspects of molecular structure influence whether a pure molecular liquid will, on cooling, form a crystal or a glass. The term "crystal engineering" was coined to describe "the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties".[2] There is a growing need for the development of similar insights into the production of amorphous solids. Since the production of the first metallic glass in 1960,[3] the central question of that field has been to understand how to chemically manipulate the properties of amorphous alloys, with glass-forming ability being the most crucial of these properties.[4] More recently, the increasing importance of obtaining amorphous phases for small organic molecules in pharmaceuticals[5] and coatings in electronic applications[6] has drawn attention to the open question of the relationship between molecular structure and glass-forming ability. The study of the variation of the glass-forming ability across an homologous series of molecules is a useful strategy for isolating the effect of specific structural features. In this paper we examine the glass-forming ability of an homologous series related to OTP, the *cyclo*-stilbenes.

There has been a considerable amount of work on the dependence of the glass transition temperature T_g on molecular size. In 1950, Fox and Flory[7] proposed the following relation for polystyrene of molecular weight M,

$$T_g = T_{g,\infty} - \frac{6.9 \times 10^4}{M} \tag{1}$$

a result that can be obtained by treating the polymer T_g as the linear combination of the T_g from two species: bulk monomer and end monomer. Equation 1 has been extended by Cowie[8] who noted that it failed to properly characterize the size dependence of T_g in short oligomers. Hintermeyer et al.[9] have argued that T_g saturates with respect to molecular weight at the onset of entanglement, a conclusion subsequently challenged by Agapov and Sokolov.[10] Angell et al.[11] noted that in small molecules the T_g tends to increase linearly with molecular size across a homologous series. Wang and Richert[12] have also found a monotonic (although nonlinear) increase in T_g with increasing molecular size for the *n*-alkanols. (Reference 12 presents an extensive collection of T_g's for a large number of homologous series in the course of exploring the relationship between T_g and the boiling point.)

The variation of T_g with molecular properties, while of considerable interest, cannot be translated directly into information about the variation of glass-forming ability. There are relatively few studies of the glass-forming ability across homologous series capable of identifying the role of specific structural variations. Alba et al.[13] exploited the superior glass-forming ability of the low melting point *m*-xylene to study the glass

Received: November 17, 2010
Revised: February 14, 2011
Published: April 05, 2011

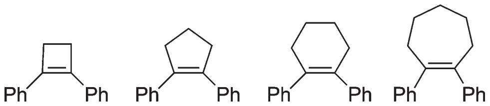


Figure 1. The four *cyclo*-stilbenes used in this study: (from left to right) 1,2-diphenylcyclobutene, 1,2-diphenylcyclopentene, 1,2-diphenylcyclohexene, and 1,2-diphenylcycloheptene, all in the cis configuration.

transition in mixtures of *m*-xylene and eithr *o*- or *p*-xylene. Whitaker and McMahon[14] reported on the glass-forming abilities of the four isomers of tris-napthylbenzene: isomers 1−3 are good glass formers, while isomer 4 is described as not forming a glass. The reason for this difference lies in the striking difference in the melting points. For isomers 1−3, T_m lies in the range 147−194 °C as compared with a T_m for isomer 4 of 238 °C. Factors that influence the anomalous stability of isomer 4 presumably include molecular symmetry and the effect (and likelihood) of rotations of the napthyl groups. Mandanici et al.[15] looked at a series of alkylcyclohexanes. They report that propylcyclohexane exhibits a significantly better glass-forming ability than the ethyl- or the butyl-substituted compounds.

OTP was identified as a good glass former by Andrews and Ubelhode[16] in 1955, and its glass transition was studied in some detail by Greet and Turnbull.[1] As already mentioned, we do not know why OTP is a good glass former. Andrews and Ubbelohde[16] suggested that the possibility of two different pair packings (head-to-head and head-to-tail) may contribute to the stability of the amorphous state. The ortho arrangement of the phenyls is certainly important since *p*-terphenyl (the linear conformation) is not a good glass former.[16] We shall therefore look at a homologous series of molecules that retains the cis conformation of phenyl rings across a double bond but varies the character of the central ring. The *cyclo*-stilbenes provide a synthetically convenient series that meets these requirements. In this study we have looked at four compounds: 1,2-diphenylcyclobutene, 1,2-diphenylcyclopentene, 1,2-diphenylcyclohexene, and 1,2-diphenylcycloheptene. The structural feature of OTP that has been retained (i.e, the cis arrangement of phenyl groups across an unsaturated bond) corresponds to the *cis*-stilbene structure (see Figure 1). The most stable isomer of stilbene is the trans configuration. The trans configuration in the *cyclo*-stilbenes requires the ring to twist and so is inaccessible for small rings. Studies of the cycloalkenes[17] have found that rings of size 8 or 9 represent the threshold above which the trans configuration is again the stable configuration. It is interesting to note that the cis to trans transition is, in the cyclo compounds, accompanied by a transformation from an open achiral ring conformation to a twisted chiral structure.

This paper is organized as follows: In Section 2 we describe the synthesis and characterization of the *cyclo*-stilbenes along with the details of the differential scanning calorimetry (DSC), large angle X-ray scattering measurements, and shear viscosity measurements reported here. In Section 3 we report our observations including the variation in glass-forming ability. In Section 4 we feed our observed data into the classical model of crystal nucleation and growth to predict the time−temperature transformation (TTT) curves and obtain estimates of the critical cooling rate in order to see what property of the molecules is most responsible for the observed variation in the glass-forming ability. Our conclusions are presented in the final section.

2. METHODOLOGY

2.1. Synthesis of Cyclic Stillbenes. The C4, C5 and C6 1,2-diphenylcycloalkenes are all known compounds, whereas the C7 is new. All four compounds were prepared by McMurray cyclization[18] of dibenzoylalkanes, using the modification of Baumstark and co-workers[19] where Ti(0) is obtained through the reduction of $TiCl_3$ with $LiAlH_4$. A typical procedure, describing the preparation of the C7 compound, is given in Appendix A.1. While Baumstark and co-workers describe the synthesis of the C8 ring via this method, we only obtained a complex mixture of hydrocarbons (^{13}C NMR analysis) from which a pure compound could not be obtained through either flash chromatography or recrystallization.

2.2. Differential Scanning Calorimetry. A Mettler Toledo DSC823^e was used to carry out the DSC. The samples (∼ 10 mg) were sealed in aluminum pans.

2.3. Determination of the Crystal Structure of 1,2-Diphenylcycloheptene. A colorless plate-like crystal of 1,2-diphenylcycloheptene was mounted in a Bruker-Nonius FR591 Kappa APEX II diffractometer employing graphite monochromated MoKα radiation generated from a fine-focus rotating anode and was used for the data collection. Cell constants were obtained from a least-squares refinement against 3704 reflections located between 5.45 and 54.53° 2θ. Data were collected at 150 K with ϕ and ω scans to 55.04° 2θ. The data integration and reduction were undertaken with SAINT and XPREP,[20] and subsequent computations were carried out with the X-Seed[21] graphical user interface. An empirical absorption correction determined with SADABS[22] was applied to the data.

The crystal structure belonged to the monoclinic space group $P2_1/c$ with lattice parameters a 12.0582(5) Å, b 5.6613(2) Å and c 20.5164(9) Å, lattice angle β 94.871(3)° and cell volume V 1395.5(1) Å^3. The unit cell contains four molecules.

3. RESULTS

In Figure 2 we present the DSC scans on heating at 10 K/min for the four cyclic stilbenes and for OTP. The melting and glass transition temperatures, T_m and T_g, respectively, obtained from the DSC data are provided in Table 1 and Figure 3. T_g is found to increase monotonically with the increasing molecular weight. While somewhat erratic, the variation of the melting point with the size of the ring is characterized by a minimum value for 1,2-diphenyl cyclohexene with a six-membered ring and an abrupt increase in T_m for the 1,2-diphenylcycloheptene. We have established that the 1,2-diphenylcycloheptene crystallizes into a monoclinic $P2_1/c$ crystal with four molecules per cell. Previous determinations[23] of the crystal structures of the cyclobutene and cyclohexene analogues reveal similar monoclinic structures with space groups $P2_1$ and $P2_1/n$, respectively, and both with four molecules per cell. The OTP crystal is orthorhombic with four molecules per unit cell. The crystal structures of the cyclic stilbenes are monoclinic rather than orthorhombic only due to small (5−10°) angular deviations from the orthrhombic.

In order to quantify the glass-forming ability, we have defined the critical cooling rate R_c, i.e., the minimum cooling rate at which any significant crystallization is avoided. The minimum cooling rate is obtained by the following procedure: A liquid is cooled at a rate R down to T_g and then heated at a fixed rate of 20 K/min. The enthalpy released upon heating is determined and taken to be proportional to the amount of crystallization

Table 1. Thermal Properties of the Four *cyclo*-Stilbenes (Where the 'Ring' Number Refers to the Number of Carbons in the Alkene Ring)[a]

	ΔH_m (kJ/mol)	T_m (K)	ΔS_m (kJ/molK)	ΔH_c (kJ/mol)	T_{rg} (= T_g/T_m)	T_g (K)	critical cooling rate R_c (K/min)
Ring4	21.34	322.5	0.06618	19.5	0.668	216	35
Ring5	21.7	328.7	0.06588	21.0	0.676	222	1.05
Ring6	17.0	317.2	0.05356	16.5	0.726	230	$\ll 0.1$
Ring7	28.6	373.7	0.07662	10.4	0.623	233	$\gg 30$
OTP	20.2	328	0.06159	20.1	0.75	246	$\ll 0.1$

[a] The analogous values for OTP are included for comparison.

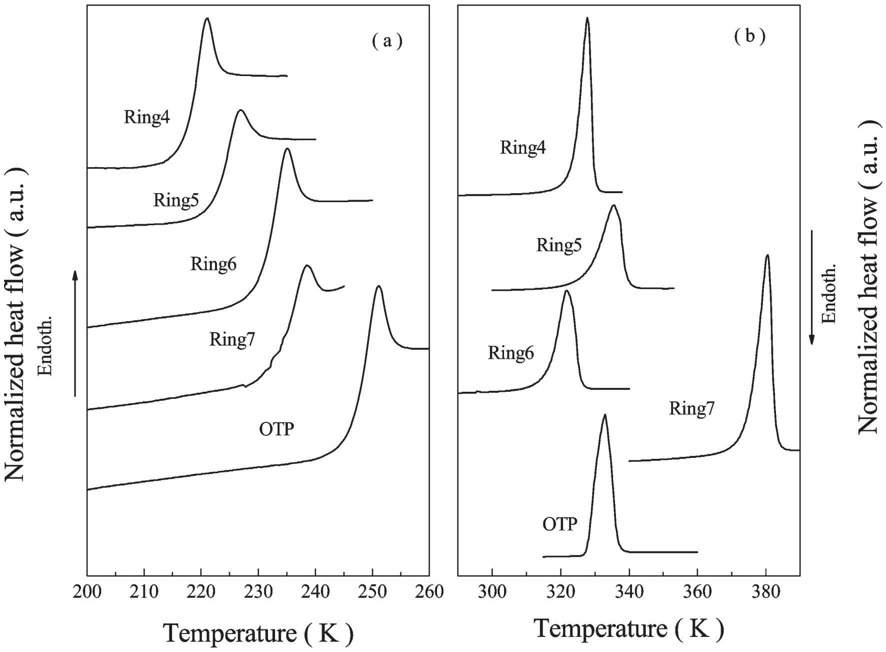


Figure 2. The DSC up scan curves of the five glassy materials prepared by a rapid liquid N_2 quench into a glass state prior to up scanning: (a) glass transition and (b) melting transition. (Crystallization occurred in the intervening temperature interval omitted from this figure.)

occurring during heating. The slower the cooling rate, the more crystallization occurs during cooling and, therefore, the less crystallization is observed during the subsequent heating stage. Consider the quantity f, defined as the ratio of the heat released upon crystallizing during the upscan divided by the heat absorbed during melting (see Figure 4). If crystallization reached completion on cooling (a "slow" cooling rate), then there is nothing left to crystallize upon heating, and $f = 0$. Likewise, after a very fast quench, all of the crystallization occurs during heating, and $f = 1$. (Here we have assumed that the crystallization processes occurring during cooling and heating result in the same total amount of crystal being formed.) The variation of f with the cooling rate is plotted in Figure 5 for each of the four stilbenes. The critical cooling rate R_c is the cooling rate at which some very small threshold amount of crystallization occurs (i.e., where f drops slightly below 1). We shall define R_c as the cooling rate at which $f = 0.95$.

The range of accessible cooling rates in this experiment is 0.1 K/min < R < 30 K/min, roughly 2.5 orders of magnitude. If the minimal cooling rate lies outside this range, then all we can do is indicate whether it lies above or below the accessible range of cooling rates. The observed critical cooling rates for the four stilbenes and OTP have been recorded in Table 1. We find a large nonmonotonic variation of R_c with the size of the alkane ring with a striking minimum in the minimal cooling rate for the six-membered ring. These results demonstrate the existence of an optimal structure with regards to glass-forming ability as we traverse the homologous series. It is worth noting that this optimal molecule is the cyclic stilbene most similar to the established glass former OTP.

The observation that T_g shows only a rather weak monotonic variation along the series suggests that the explanation of the dramatic nonmonotonic variation in the minimal cooling rate is not due to variations in the relaxation kinetics of the supercooled liquid but rather due to variation in the stability of the crystal. This conclusion is supported by previous work on xylene isomers. In the case of the isomer series *o*-, *m*-, and *p*-xylene, in which all members have closely similar viscosities, boiling points, and glass transition temperatures (and hence cohesive energies), it is known[24] from precise thermodynamic data that the difference in melting points that makes the *m*-isomer the best glass former originates in a small (4 kJ/mol) difference in the crystal lattice energies. While it is reasonable to ascribe differences in lattice energy with differences in the efficiency of molecular packing, there many open questions concerning the relationship between molecular shape and lattice stability. Considering, then, the thermodynamics of the freezing transitions of our cyclic stilbene series, we find that the melting point T_m and the

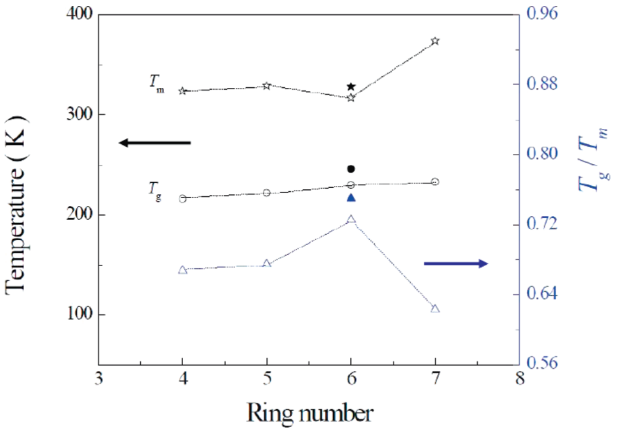


Figure 3. The dependence of T_m (top curve), T_g (middle curve), and T_g/T_m (bottom curve, right-hand axis) on the ring number of the *cyclo*-stilbenes. The data for OTP is also included (at a ring number of 6) as filled symbols.

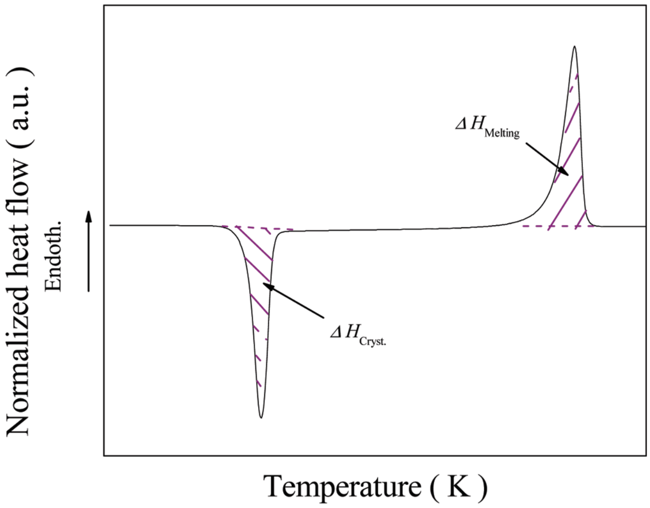


Figure 4. A schematic of a DSC upscan. The enthalpies of crystallization ΔH_{cryst} and of melting ΔH_{melt} are indicated as the areas of the respective peaks.

enthalpy of fusion ΔH_f exhibit a similar monotonic behavior with minima for the 1,2-diphenylcyclohexene. In light of the similarity of the crystal structures, it is tempting to ascribe this minimum in ΔH_f to a lower enthalpy of the liquid state at coexistence. (The subsequent discussion, however, does not rely on this suggestion.) We shall next examine whether the variations in T_m and ΔH_f across the series can account for the observed variation in the minimum cooling rate.

4. WHAT PHYSICAL QUANTITIES DETERMINE THE CRITICAL COOLING RATE?

In 1958, Turnbull and Cohen[25] proposed that any liquid could, in principle, form a glass. (There was scepticism at the time as one prevailing view held that the short-range order of most liquids was only trivially distorted from that of the crystal, and, therefore, avoidance of crystallization would not generally be possible.) The crucial role of the rate of cooling in glass formation was clearly formulated subsequently by Turnbull[26] and Uhlmann.[27] A sufficient condition for the formation of a glass is that a liquid can be cooled fast enough to avoid the formation of crystalline nuclei. This condition is more stringent than necessary since the presence of nuclei is tolerable as long as their growth rate is slow enough to result in negligible transformation. Applying this less stringent condition and using the classical expressions for the nucleation frequency and crystal growth rate, we can (following Uhlmann[27]) derive an expression for the minimum cooling rate necessary to avoid crystallization and achieve a glass that depends only on a small number of material quantities:

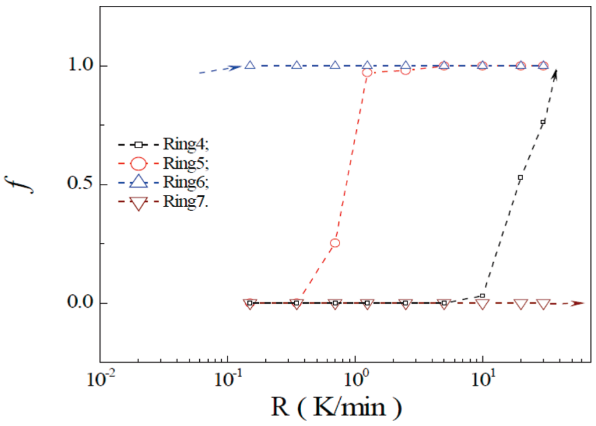


Figure 5. The ratio f (defined in the text) plotted against the cooling rate R for the four stilbene molecules. Curves that remain fixed at $f = 1$ or 0 for all cooling rates indicate a compound whose critical cooling rate lies below or above, respectively, the accessible range of cooling temperatures.

- T_m and T_g, the melting and glass transition temperatures
- ΔH_f, the molar entropy change at melting
- η, the viscosity for $T_g \leq T \leq T_m$
- the liquid density and molecular diameter

Assuming that the rate of nucleation and the crystal growth rate are, for a given temperature, both constant with time (i.e., transients and history dependence is ignored), then the volume fraction, X, crystallized in time t can, for small X, be written[27] as

$$X \approx \frac{1}{3}\pi I_v u^3 t^4 \tag{2}$$

where I_v is the nucleation frequency per unit volume and u is the rate of advance of the crystal interface per unit area. If we choose some small value of X, say 10^{-8}, to define the point at which crystallization has "occurred" then eq 2, when coupled to expressions for I_v and u in terms of the temperature, provides us with a relation between supercooling and crystallization time, the so-called TTT curve.

Using Turnbull's expression[26] for the steady-state nucleation rate per unit volume I_v, we have

$$I_v = \frac{c}{\eta}\exp[-b\alpha^3\beta/T_r(\Delta T_r)^2] \tag{3}$$

where

$$c = \frac{kT}{3\pi a_o^3} \tag{4}$$

$$\alpha = \frac{(NV^2)^{1/3}\sigma}{\Delta H_f} \tag{5}$$

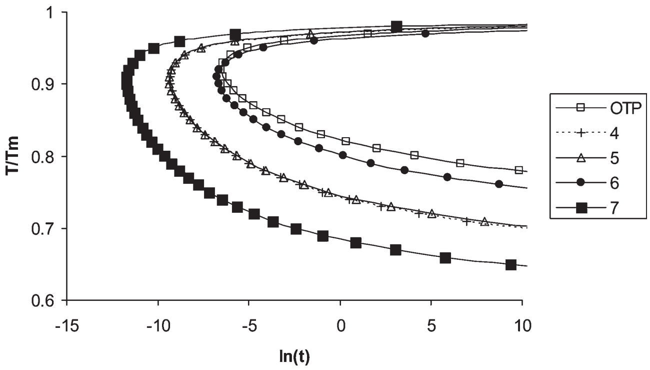


Figure 6. Calculated TTT curves for the four *cyclo*-stilbenes and OTP as explained in the text.

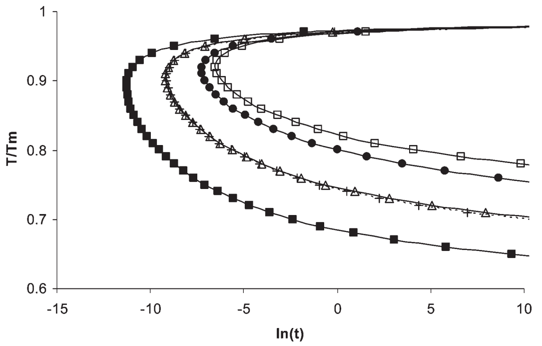


Figure 7. Calculated TTT curves for which the same enthalpy change on fusion ΔH_f (i.e., that for OTP) has been used for all compounds. The only difference between the curves was the different values of T_g/T_m used.

$$\beta = \frac{\Delta H_f}{RT_m} = \frac{\Delta S_f}{R} \tag{6}$$

and a_o is the molecular diameter, b is a parameter dependent on the shape of the nuclei (we shall assume the value $16\pi/3$ for a sphere), σ is the interfacial free energy per unit area, and η is the shear viscosity. The reduced temperature is $T_r = T/T_m$ and the reduced supercooling is $\Delta T_r = 1 - T_r$. The crystal growth rate u is given by the Wilson–Frenkel expression[27]

$$u = \frac{c}{\eta}\left[1 - \exp\left(-\frac{\Delta H_f \Delta T_r}{RT}\right)\right] \tag{7}$$

For the interfacial tension σ, we shall use a phenomenological expression recently proposed by Laird[28]

$$\sigma = 0.5RT_m/(V^{2/3}N_A) \tag{8}$$

Substituting eq 8 into eq 5 results in $\alpha = 1/(2\beta)$. We have very little data on the temperature dependence of the shear viscosity of the cyclo stilbenes and so shall assume that their viscosities obey the same Volger–Fulcher–Tamman expression as that for OTP,[1] i.e.,

$$\eta = 4.65 \times 10^{-5} \exp\left[\frac{689}{T - 231}\right] \quad \text{in units of Pas} \tag{9}$$

except that the characteristic temperature T_o is adjusted by observed calorimetric T_g of each of the stilbenes. Specifically, we find for OTP that $T_o = T_g - 15$K. We have used this same expression to estimate the value of T_o for each of the stilbenes. Finally, we have used $a_o = 10$ Å for all the molecules.

Using eqs 3–9 we have calculated TTT curves for the four cyclo stilbenes and for OTP. The results are plotted in Figure 6. We find that the "noses" of the TTT curve occurs at $T_r = 0.9$ for all the molecules, and that 1,2-diphenylcyclohexene does indeed represent a minimum in the critical cooling rate from among the homologous series. This means that our observations concerning R_c are consistent with the predictions of the standard theory and, therefore, we can use the theory to identify what physical quantity or quantities determined the glass-forming behavior. In Figure 7 we have recalculated the TTT curves but, this time, replaced the actual values of ΔH_f for each molecule with a single value (that for OTP). Having removed the difference in heats of fusion, we find little qualitative change in the TTT curves, with 1,2-diphenylcyclohexene, in particular, retaining its position as the optimal glass former. On the basis of these results, we conclude that the glass-forming ability across the *cyclo*-stilbene series is determined by the value of the only other material parameter remaining, i.e., T_o/T_m or, more generally, the reduced glass transition temperature T_g/T_m. This conclusion is consistent with Turnbull's 1969 proposal[26] that the reduced glass transition temperature provides a good predictor of glass-forming ability.

The significance of T_g/T_m with regards the glass-forming ability needs some qualification. Glass-forming ability is determined by the position of the "nose" of the TTT curve. Since this nose occurs at temperatures well above T_g, it is clear that the value of T_g really has no direct influence on glass-forming ability. What actually matters is the growth in viscosity over supercoolings down to $T/T_m \sim 0.9$. The quantity T_g/T_m enters here simply to the extent that the reduced glass transition temperature provides a convenient parametrization of the viscosity increase over these small supercoolings.

5. DISCUSSION

In this paper we have shown that the glass-forming ability of molecules related structurally to OTP changes nonmonotonically as one moves across the homologous series. In particular, we found that 1,2-diphenylcyclohexene (the member of the series most like OTP) has a considerably higher glass-forming ability (i.e., smaller minimum cooling rate) than molecules smaller and larger than it in the series. Calculations of the TTT curves using classical nucleation theory and the Wilson–Frenkel theory of crystal growth rate were able to reproduce the observation that 1,2-diphenylcyclohexene was the optimal glass former in the homologous series of cyclic stilbenes. Using these calculations, we showed that the physical quantity responsible for this trend was the ratio T_g/T_m. The good glass formers (OTP and 1,2-diphenylcyclohexene) have a high reduced glass transition temperature T_g/T_m (0.73 for 1,2-diphenylcyclohexene and 0.75 for OTP), while for the poorer glass formers this value is below 0.68. While glass-forming ability is the specific focus of this paper, we do note that the actual value of T_g is also an important consideration. For OTP, $T_g = 246$ K, significantly higher than any of the stillbenes studied here. In terms of this discussion, this high T_g for OTP arises from the dual influences of a high melting point and the high glass-forming ability shared with the cyclic stilbene with a six membered ring.

Kauzman[29] and Turnbull[26] suggested that good glass forming depended on $T_g/T_m > 2/3$. While our results concur with the significance of the reduced glass transition temperature, the threshold vale of 2/3 appears to be lower bound on the threshold for good glass-forming ability since we find examples of poor glass formers with $T_g/T_m \sim 2/3$. Alba-Simionesco et al.[30] pointed out that the empirical 2/3 "rule" may simply reflect the fact that T_m values become scarce when the material is too good a glass former, hence reducing the number of examples of large values of T_g/T_m in the literature.

In 1958, Turnbull and Cohen[25] proposed that the ratio of boiling point T_b over melting point T_m provided a useful predictor of glass-forming ability, with $T_b/T_m > 2$ being a mark of a good glass former. This approach completely discards any information about the temperature dependence of the relaxation kinetics of the glass in favor of focusing on the stability of the crystal. As is argued by Angell et al.,[24] since T_b provides a measure of the strength of the cohesive energy between molecules in the liquid, a T_m that falls below the $T_b/2$ threshold is an indication of a poor crystal whose packing does not allow the molecules to extract the usual stability from the attractive interactions in the crystal.

The quest for a clear quantitative predictor of glass-forming ability (i.e., the position of the "nose" on the TTT curve) has been most seriously pursued in the metallic glass community. This pursuit has produced a small crowd of measures[4] in addition to the reduced glass transition temperature T_g/T_m. Many of these measures make use of the onset crystallization temperature T_x, defined as the temperature at which crystallization is first observed during heating (at some standard rate) from the glass.[31] T_x provides information about the stability of the glass state with respect to crystallization. While not directly connected to the cooling process (there is a strong likelihood that a sample quenched to its glass transition will have acquired a distribution of potential crystal nuclei that will strongly influence the onset crystallization temperature on heating), the idea[4] is that the likelihood of forming a glass should be related to the subsequent stability of that glass.

Suryanarayana et al.[4] compared a number of measures of glass-forming ability against the maximum diameters at which fully glass material can be obtained on quenching (related to the critical cooling rate) for a large number of metallic glass formers. Good correlations were found between some measures and certain families of amorphous alloys. Most criteria worked well for Nd- and Au-based alloys. The reduced glass temperature T_g/T_m alone correlated well with the glass-forming ability of Co-based alloys. Overall, however, none of the proposed measures were found to provide a convincing prediction of glass-forming ability. Remarkably, there were cases like the commercially important Zr-based alloys, which exhibited little variation in their (excellent) glass-forming ability despite exploring values for T_g/T_m ranging from 0.5 to 0.7.

The survey presented in ref 4 raises an important issue. It is quite possible that a number of different mechanisms are responsible for glass stability, and that no single parameter can capture all of these. For example, in concluding that T_g/T_m determined glass-forming ability, we have used a simple correlation between crystal—liquid interfacial free energy and the melting temperature. Compounds for which this rule does not hold can show strong deviations from this simple scaling. Such considerations underlie the value of looking for predictors of glass-forming ability just within homologous series so as to avoid trying to compare what may be quite different stabilizing effects.

We began this paper pointing out the need for a level of understanding in the molecular determination of glass-forming ability analogous to that sought for crystals under the banner of crystal engineering. We conclude this paper with the observation that the molecular determination of glass-forming ability may be best thought of as another branch of crystal engineering since the clearest determinant of glass-forming ability is to be found in the stability (relative to the glass transition) of the crystal. The *cyclo*-stilbene results we have presented here underline the fact that even a 5% variation in T_m can have a significant effect on the glass-forming ability. This observation, along with the evidence in the literature[14] of minor changes in a molecule structure resulting in large changes in T_m, emphasizes the subtlety of the challenge of understanding the connection between molecular structure and crystal stability to the level that allows prediction of glass-forming ability.

APPENDIX

A1. Further Details of the Synthesis of the *cyclo*-Stilbenes

1,3-Dibenzoylpropane and 1,4-dibenzoylbutane were obtained from Aldrich and used as received. 1,2-Dibenzoylethane and 1,5-dibenzoylpentane were prepared by the Friedel-Crafts acylation of benzene with the corresponding diacid chlorides, using the procedure described by Fuson and Walker.[32] 1,2-Dimethoxyethane was obtained from Aldrich and dried statically over 4A molecular sieves for several days prior to use. All other reagents were obtained from Aldrich and used as received. Flash chromatography was carried out using Scharlau GE 0048 Silica Gel 60, 0.04-0.06 mm (230-400 mesh ASTM).

The synthesis of 1,2-diphenylcycloheptene (see Figure A1) proceeded as follows. $LiAlH_4$ (0.68 g, 18 mmol) was added to $TiCl_3$ (6.5 g, 42 mmol) in dry 1,2-dimethoxyethane (250 mL) under Ar. The mixture was heated under reflux for 15 min. Solid 1,5-dibenzoylpentane (2.3 g, 8.1 mmol) was then added in one portion to the cool reaction mixture and then heating under reflux resumed for 48 h. The cool reaction mixture was poured into hexane followed by the addition of water. The organic phase was separated, washed with water, dried over $MgSO_4$, and the solvent was then removed under reduce pressure. The residue was then purified by flash chromatography, eluting with hexane (product $R_f = 0.5$). Recrystallization from ethanol afforded the pure cycloheptene as colourless plates (260 mg, 13% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 1.72−1.75 (m, 4H), 1.92−1.94 (m, 2H), 2.70−2.73 (m, 4H), 6.96−7.11 (m, 10H).

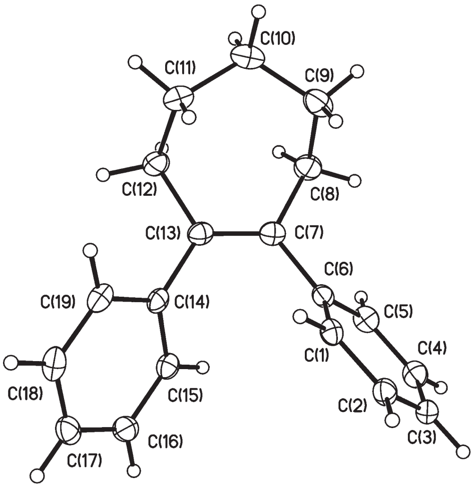


Figure A1. ORTEP plot of 1,2-diphenylcycloheptene with crystallographic numbering. Non-hydrogen atoms are shown with thermal ellipsoids at 50% probability.

^{13}C NMR (125 MHz, $CDCl_3$) δ 26.7 ($2CH_2$), 32.7 (CH_2), 36.8 ($2CH_2$), 125.4 (2CH), 127.5 (4CH), 128.9 (4CH), 141.0 (2C), 145.2 (2C).

A2. Further Details of the Structure Determination of the 1,2,-Diphenylcycloheptene Crystal. The colourless plate-like crystal was attached with Exxon Paratone N, to a short length of fibre supported on a thin piece of copper wire inserted in a copper mounting pin. The crystal was quenched in a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. A Bruker-Nonius FR591 Kappa APEX II diffractometer employing graphite monochromated MoKα radiation generated from a fine-focus rotating anode was used for the data collection. Cell constants were obtained from a least squares refinement against 3704 reflections located between 5.45 and 54.53° 2θ. Data were collected at 150(2) Kelvin with ϕ and ω scans to 55.04° 2θ. The data integration and reduction were undertaken with SAINT and XPREP, and subsequent computations were carried out with the X-Seed graphical user interface. An empirical absorption correction determined with SADABS was applied to the data.

The structure was solved in the space group $P2_1/c$(#14) by direct methods with SHELXS-97, and extended and refined with SHELXL-97. The non-hydrogen atoms in the asymmetric unit were modelled with anisotropic displacement parameters. A riding atom model with group displacement parameters was used for the hydrogen atoms.

Formula $C_{19}H_{20}$, $M = 248.35$, Monoclinic, space group $P2_1/c$(#14), $a = 12.0582(5)$, $b = 5.6613(2)$, $c = 20.5164(9)$ Å, $\beta = 94.871(3)$, $V = 1395.5(1)$ Å^3, $D_c = 1.182$ g cm^{-3}, $Z = 4$, crystal size = 0.37 × 0.14 × 0.01 mm, colour = colorless, habit plate, temperature = 150(2) K, λ(MoKα) = 0.71073 Å, μ(MoKα) = 0.066 mm^{-1}, $T(\mathrm{SADABS})_{\mathrm{min,max}} = 0.933, 0.999$, $2\theta_{\mathrm{max}} = 55.04$, hkl range = −15 15, −7 7, −24 26; $N = 12282$, $N_{\mathrm{ind}} = 3201$($R_{\mathrm{merge}} = 0.0273$), $N_{\mathrm{obs}} = 2398(I > 2\sigma(I))$, $N_{\mathrm{var}} = 172$, residuals [$R1 = \Sigma||F_o| - |F_c||/\Sigma||F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections $w = 1/[\sigma^2(F_o^2) + (0/0368P)^2 + 0.4519P]$ where $P = (F_o^2 + 2F_c^2)/3$] $R1(F)$ 0.0394, $wR2(F^2)$ 0.0937, GoF(all) 1.007, $\Delta\rho_{\mathrm{min,max}}$ −0.173, 0.230 e$^-$ Å^{-3}.

■ ACKNOWLEDGMENT

We gratefully acknowledge support from the Australian Research Council.

■ REFERENCES

(1) Greet, R. J.; Turnbull, D. *J. Chem. Phys.* **1967**, *46*, 1243.

(2) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: New York, 1989).

(3) Klement, W.; Willens, R. H.; Duwez, P. *Nature* **1960**, *187*, 869.

(4) Suryanarayana, C.; Seki, I.; Inoue, A. *J. Non-Cryst. Solids* **2009**, *355*, 355.

(5) Yu., L. *Adv. Drug Delivery Rev.* **2001**, *48*, 27.

(6) Dimitrakopoulos, C. D.; Mascaro, D. J. *IBM J. Res. Dev.* **2001**, *45*, 11. Choo, B.-K.; Choi, J.-S.; Kim, S.-W.; Park, K.-C.; Jang, J. *J. Non-Cryst. Solids* **2006**, *352*, 1704.

(7) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.

(8) Cowie, J. M. G. *Eur. Polym. J.* **1975**, *11*, 297.

(9) Hintermeyer, J.; Herrmann, A.; Kahlau, R.; Goiceanu, C.; Rössler, E. A. *Macromolecules* **2008**, *41*, 9335.

(10) Agapov, A. L.; Sokolov, A. P. *Macromolecules* **2009**, *42*, 2877.

(11) Angell, C. A.; Sare, J. M.; Sare, E. J. *J. Phys. Chem.* **1978**, *82*, 2622.

(12) Wang, L.-M.; Richert, R. *J. Phys. Chem. B* **2007**, *111*, 3201.

(13) Alba, C.; Busse, L. E.; List, D. J.; Angell, C. A. *J. Chem. Phys.* **1990**, *92*, 617.

(14) Whitaker, C. M.; McMahon, R. J. *J. Phys. Chem.* **1996**, *100*, 1081.

(15) Mandanici, A.; Cutroni, M.; Triolo, A.; Rodriguez-Mora, V.; Ramos, M. A. *J. Chem. Phys.* **2006**, *125*, 054514.

(16) Andrews, J. N.; Ubbelohde, A. R. *Proc. R. Soc. (London)* **1955**, *A228*, 435.

(17) Inoue, Y.; Yokoyama, T.; Yamasaki, N.; Tai, A. *Nature* **1989**, *341*, 225.

(18) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255.

(19) Baumstark, A. L.; McCloskey, C. J.; Witt, K. E. *J. Org. Chem.* **1978**, *43*, 3609.

(20) *SMART, SAINT, and XPREP. Area Detector Control and Data Integration and Reduction Software*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1995.

(21) Barbour, L. J. *J. Supramol. Chem.* **2001**, *1*, 189.

(22) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(23) Hohlneicher, G.; Müller, M.; Demmer, M.; Lex, J.; Penn, J. H.; Gan, L.; Loesel, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 4483.

(24) Angell, C. A.; Busse, L. E.; Cooper, E. E.; Kadiyala, R. K.; Dworkin, A.; Ghelfenstein, M.; Szwarc, H.; Vassal, A. *J. Chim. Phys.* **1985**, *82*, 267.

(25) Turnbull, D.; Cohen, M. H. *J. Chem. Phys.* **1958**, *29*, 1049.

(26) Turnbull, D. *Contemp. Phys.* **1969**, *10*, 473.

(27) Uhlmann, D. R. *J. Non-Cryst. Solids* **1972**, *7*, 337.

(28) Laird, B. *J. Chem. Phys.* **2001**, *115*, 2889.

(29) Kauzman, W. *Chem. Rev.* **1948**, *43*, 219.

(30) Alba-Simionesco, C.; Fan, J.; Angell, C. A. *J. Chem. Phys.* **1999**, *110*, 5262.

(31) Lu, Z. P.; Liu, C. T. *Phys. Rev. Lett.* **2003**, *91*, 115505.

(32) Fuson, R. C.; Walker, J. T. *Organic Syntheses*; Wiley: New York, 1943; Vol. 2, p 169.