JOURNAL OF Materials CHEMISTRY

Stable low molecular weight glasses based on mixtures of bisphenol-A and bispyridines

Sylvie Boileau,[a] Laurent Bouteiller,*[a,b] Eric Foucat[a] and Nelly Lacoudre[a]

[a]*Laboratoire de Recherche sur les Polymères, UMR C7581, CNRS, 2 rue Henri Dunant, BP 28, 94320 Thiais, France*
[b]*Laboratoire de Chimie Macromoléculaire, UMR 7610, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris cedex 05, France. Tel: +33-1-44-27-73-78; Fax: +33-1-44-27-70-89; E-mail: bouteil@ccr.jussieu.fr*

Received 13th July 2001, Accepted 8th November 2001
First published as an Advance Article on the web 17th December 2001

Low molecular weight organic glasses were made by melt mixing two crystalline solids: bisphenol A and various bispyridines. Stable glasses were obtained because of intermolecular hydrogen bond formation between phenol and pyridine groups. The composition dependence of the *T*g of the mixtures shows a very strong and positive deviation from the behavior of ideal copolymers or ideal polymer blends. Moreover, the strong influence of the structure of the low molecular weight compounds on the *T*g of the mixture can be adequately described by empirical relationships, which are known in the field of polymers.

Introduction

The use of low molecular weight hydrogen bond donors with hydrogen bond acceptors is well known in the field of supramolecular chemistry. As far as condensed matter is concerned, the directionality of hydrogen bonding has been exploited to enforce a particular arrangement of components in crystals[1] or in liquid crystals.[2] However, hydrogen bonding in two component mixtures of low molecular weight compounds has not been used to stabilize the glassy state.

As a matter of fact, low molecular weight organic glasses are increasingly investigated because they potentially combine several interesting properties such as easy purification, good processability and high guest solubility.[3] Numerous applications are envisaged, for example in light emitting devices (as emitting layer[4] or as charge transporting layer[5]), in non-linear optics,[6] in optical data storage,[7] and in photovoltaic and photochromic materials.[8] Consequently, the influence of the molecular structure on stability of the glass and on the value of the glass transition temperature is an important question.

It is well recognized that shape irregularity is essential to obtain a stable glass and that rigidity and intermolecular interactions increase the *T*g value, but most experimental studies have been focused on single component low molecular weight glasses.[9,10] This paper demonstrates the increased stability of the glass obtained by mixing two compounds and the beneficial effect of intermolecular hydrogen bonding on *T*g.

Experimental

Analysis

Glass transition temperatures (*T*g) were measured using a Perkin–Elmer DSC 4 instrument. Samples were first cooled to a temperature about 50 °C below their *T*g, then heated at a heating rate of 20 °C min^{-1} (unless otherwise mentioned) and quenched again. The cycle was repeated at least once, and the *T*g value was taken as the onset of the specific heat increment of the second heating curve. The standard error was estimated to be less than ±2 °C by preparing some mixtures three times and measuring the *T*g at least twice for each mixture. Infrared spectra were recorded at room temperature on a Perkin–Elmer FTIR 1760 spectrometer and ^{1}H and ^{13}C NMR spectra were recorded on a AC 200-e Bruker spectrometer.

Synthesis

Compounds **1** (97%, Aldrich), **3** (99%, Janssen Chimica) and **4** (97%, Aldrich) were used as received (Fig. 1). Bispyridine **2** (98%, Aldrich) was recrystallized from a mixture of cyclohexane and hexane.

Bispyridine 5

See Scheme 1. In a round-bottomed flask, 8.8 g (64 mmol) of 4-(3-hydroxypropyl)pyridine (98%, Aldrich), 9 ml (64 mmol) of triethylamine (Merck, distilled over KOH) and 50 ml of tetrahydrofuran (THF, stored over molecular sieves) were introduced and cooled at 0 °C. Under nitrogen and through a dropping funnel, 3.5 ml (32 mmol) of butanedioic acid dichloride (95%, Aldrich) in 50 ml of THF were added dropwise. After the addition, the reaction mixture was allowed to reach room temperature and was stirred overnight. After filtration, THF was evaporated and the residue was dissolved in dichloromethane and extracted with a saturated $NaHCO_3$ solution and then with water. The organic phase was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography on silica gel with an ethyl acetate–ethanol mixture as the eluent. Yield: 40%, mp 60 °C. ^{1}H NMR ($CDCl_3$, ppm) δ: 8.45–7.08 (2d, 8H, pyridyl),

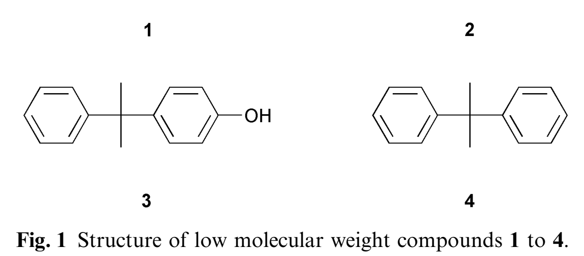
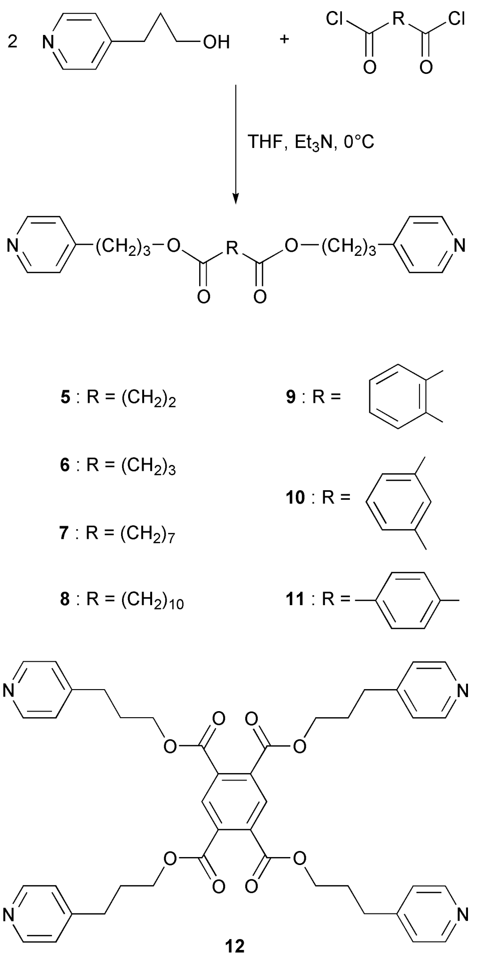


Fig. 1 Structure of low molecular weight compounds **1** to **4**.



Scheme 1 Synthesis of bispyridines **5** to **11** and tetrapyridine **12**.

4.07 (t, 4H, CH_2-O), 2.65 (t, 4H, CH_2-Ar), 2.58 (s, 4H, CH_2-C=O), 1.92 (p, 4H, CH_2-CH_2-Ar). FTIR $\nu_{C=O}$: 1740 cm^{-1}.

Bispyridine 6

The same procedure as for **5** was used with 3.7 ml (29 mmol) of pentanedioic acid dichloride (97%, Aldrich). Yield: 10% of a liquid. ^{1}H NMR ($CDCl_3$, ppm) δ: 8.48–7.08 (2d, 8H, pyridyl), 4.07 (t, 4H, CH_2-O), 2.65 (t, 4H, CH_2-Ar), 2.35 (t, 4H, CH_2-C=O), 1.95 (m, 4H, CH_2-CH_2-Ar), 1.95 (m, 2H, CH_2-CH_2-C=O). FTIR $\nu_{C=O}$: 1740 cm^{-1}.

Bispyridine 7

The same procedure as for **5** was used with 6.9 g (31 mmol) of nonanedioic acid dichloride (98%, Aldrich). Yield: 50% of a liquid. ^{1}H NMR ($CDCl_3$, ppm) δ: 8.46–7.07 (2d, 8H, pyridyl), 4.05 (t, 4H, CH_2-O), 2.64 (t, 4H, CH_2-Ar), 2.26 (t, 4H, CH_2-C=O), 1.94 (p, 4H, CH_2-CH_2-Ar), 1.58 (m, 4H, CH_2-CH_2-C=O), 1.30 (m, 6H, $(CH_2)_3$-CH_2-CH_2-C=O). FTIR $\nu_{C=O}$: 1740 cm^{-1}.

Bispyridine 8

The same procedure as for **5** was used with 4.1 ml (16 mmol) of dodecanedioic acid dichloride (98%, Aldrich). Yield: 45%, mp 48 °C. ^{1}H NMR ($CDCl_3$, ppm) δ: 8.46–7.08 (2d, 8H, pyridyl), 4.05 (t, 4H, CH_2-O), 2.65 (t, 4H, CH_2-Ar), 2.24 (t, 4H, CH_2-C=O), 1.92 (p, 4H, CH_2-CH_2-Ar), 1.57 (m, 4H, CH_2-CH_2-C=O), 1.24 (m, 12H, $(CH_2)_6$-CH_2-CH_2-C=O). FTIR $\nu_{C=O}$: 1740 cm^{-1}.

Bispyridine 9

The same procedure as for **5** was used with 4.1 ml (28 mmol) of phthaloyl chloride (Aldrich). Yield: 45% of a liquid. ^{1}H NMR ($CDCl_3$, ppm) δ: 8.45–7.09 (2d, 8H, pyridyl), 7.65–7.52 (2m, 4H, C_6H_4), 4.29 (t, 4H, CH_2-O), 2.70 (t, 4H, CH_2-Ar), 2.03 (p, 4H, CH_2-CH_2-Ar). FTIR $\nu_{C=O}$: 1725 cm^{-1}.

Bispyridine 10

The same procedure as for **5** was used with 5.7 g (28 mmol) of isophthaloyl chloride (98%, Aldrich). Yield: 35%, mp 44 °C. ^{1}H NMR ($CDCl_3$, ppm) δ: 8.63–8.15–7.51 (s–d–t, 4H, C_6H_4), 8.46–7.11 (2d, 8H, pyridyl), 4.36 (t, 4H, CH_2-O), 2.76 (t, 4H, CH_2-Ar), 2.12 (p, 4H, CH_2-CH_2-Ar). FTIR $\nu_{C=O}$: 1725 cm^{-1}.

Bispyridine 11

The same procedure as for **5** was used with 5.1 g (25 mmol) of terephthaloyl chloride (99%, Aldrich). Yield: 50%, mp 89 °C. ^{1}H NMR ($CDCl_3$, ppm) δ: 8.52–7.15 (2d, 8H, pyridyl), 8.03 (s, 4H, C_6H_4), 4.39 (t, 4H, CH_2-O), 2.80 (t, 4H, CH_2-Ar), 2.15 (p, 4H, CH_2-CH_2-Ar). FTIR $\nu_{C=O}$: 1725 cm^{-1}.

Tetrapyridine 12

The same procedure as for **5** was used with 10.8 g (79 mmol) of 4-(3-hydroxypropyl)pyridine and 6.4 g (19 mmol) of 1,2,4,5-benzenetetracarboxylic acid tetrachloride.[11] Yield: 30%, mp 114 °C. ^{1}H NMR ($CDCl_3$, ppm) δ: 8.47–7.09 (2d, 16H, pyridyl), 7.99 (s, 2H, C_6H_2), 4.35 (t, 8H, CH_2-O), 2.71 (t, 8H, CH_2-Ar), 2.07 (p, 8H, CH_2-CH_2-Ar). FTIR $\nu_{C=O}$: 1725 cm^{-1}.

Sample preparation

Mixtures of bisphenols and bispyridines were obtained by weighing the desired quantities of each compound in a small vial and melting under magnetic stirring for a few minutes at 170 °C.

Results and discussion

Bisphenol–bispyridine mixtures

It is well known that phenols form reasonably strong hydrogen bonds with pyridines. Consequently, commercially available bisphenol A **1** and bispyridine **2** (Fig. 1) were chosen to investigate the effect of hydrogen bonding on the glass stability. Compounds **1** and **2** are crystalline solids, which melt at 152 °C and 61 °C respectively. If **1** is melted and then quenched, its DSC heating curve displays a glass transition ($Tg_1 = 36$ °C), an exotherm due to crystallization ($Tc_1 = 72$ °C) and finally an endotherm due to melting ($Tm_1 = 152$ °C) (Fig. 2). Similarly, if **2** is melted and then quenched, its DSC heating curve displays a glass transition ($Tg_2 = -71$ °C, not shown), a crystallization exotherm ($Tc_2 = -40$ °C, not shown) and a melting endotherm ($Tm_2 = 61$ °C). Unlike the pure compounds, if **1** and **2** are mixed in an equimolar ratio and melted, a transparent glass is obtained. Fig. 2 shows that the only feature of the DSC heating scan is a glass transition at 9 °C. The stability of the glass was assessed by reducing the heating rate, thereby giving more time for the super-cooled melt to crystallize. Fig. 3 shows that it is possible to detect the Tg down to a heating rate of 1 °C min^{-1}, but that even at this low rate, no crystallization occurs.

The presence of hydrogen bonds was investigated by FTIR spectroscopy. The spectrum of pure bisphenol A **1** shows a wide absorption band around 3320 cm^{-1} indicative of hydrogen bond formation between phenol functions.[12] However, in the case of the equimolar mixture of **1** and **2**, the absorption band is shifted to 3030 cm^{-1} proving that phenol groups are hydrogen bonded to pyridine groups.[12] The formation of these

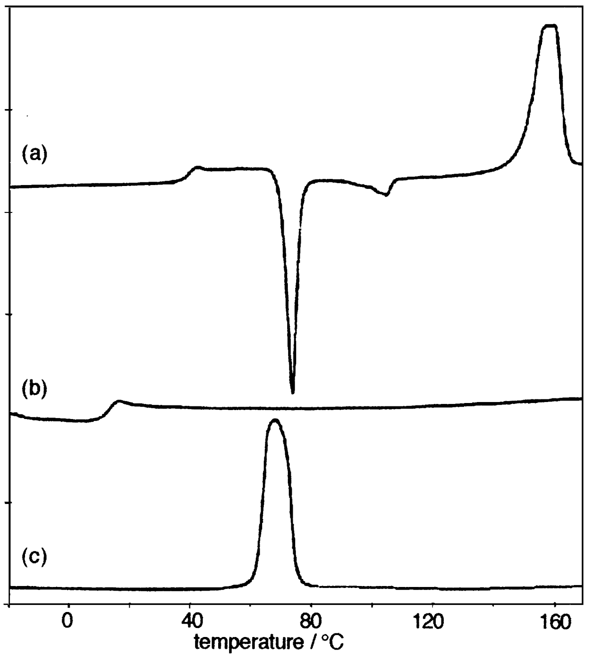


Fig. 2 DSC thermograms of bisphenol A **1** (a), bispyridine **2** (c) and their equimolar mixture (b). Heating rate: 20 °C min^{-1}.

strong hydrogen bonds is certainly responsible for the stability of the glass.

Influence of stoichiometry

The glass transition temperature of mixtures of **1** and **2** in varying proportions was measured and is represented by black squares on Fig. 4, *versus* the weight fraction of bisphenol (w). The corresponding continuous curve is drawn according to the Fox equation:

$$\frac{1}{Tg} = \frac{w}{Tg_1} + \frac{1-w}{Tg_2} \tag{1}$$

The Fox equation is considered to describe the composition dependence of the Tg of ideal copolymers or ideal polymer blends in which no strong interactions are involved. In the present case, mixtures of **1** and **2** show a very strong and positive deviation from the Fox equation. The maximum deviation is of 40 °C, which is probably due to hydrogen bonding between the two components. To check that the deviation from the Fox equation is due to hydrogen bonding, two model compounds (**3** and **4**) were used. Compounds **1**, **3** and **4** (Fig. 1) have similar structures, but **3** bears only one phenol group and **4** has none. The Tg of the mixtures of **3** with **2** also shows a positive deviation from the Fox equation (Fig. 4), however this deviation is smaller than for mixtures of **1** with **2**. In the case of **4**, which cannot form any hydrogen bonds, the deviation from the Fox equation is negligible (Fig. 4). These data confirm that the unusually strong deviation of the Tg of mixtures of **1** with **2** is due to hydrogen bonding between phenol and pyridine groups.

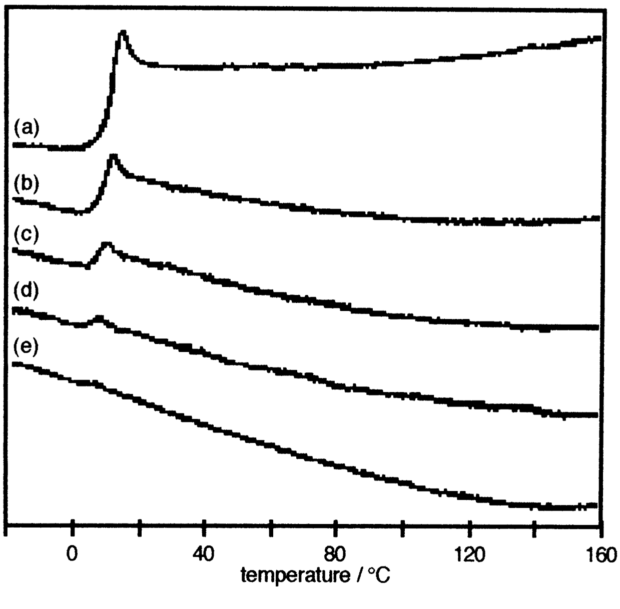


Fig. 3 DSC thermograms of the equimolar mixture of bisphenol A **1** with bispyridine **2** for several heating rates: 20 °C min^{-1} (a), 10 °C min^{-1} (b), 5 °C min^{-1} (c), 2.5 °C min^{-1} (d), and 1 °C min^{-1} (e).

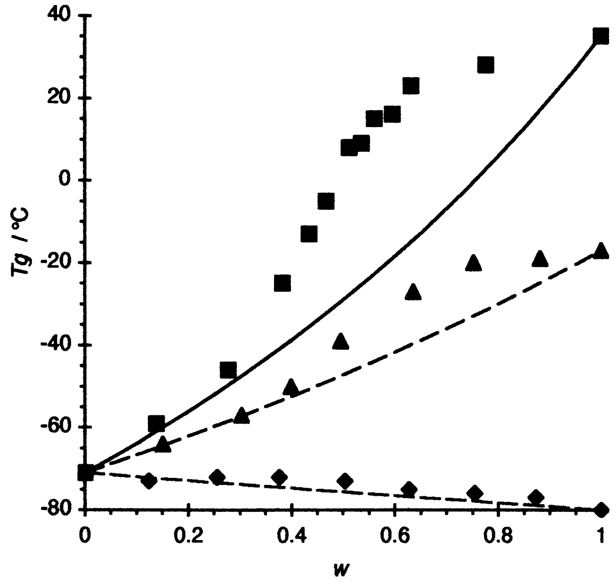


Fig. 4 Glass transition temperature (Tg) of mixtures of bispyridine **2** with bisphenol A **1** (■), monophenol **3** (▲) and compound **4** (◆) *versus* weight fraction of the second component (w). The curves are drawn according to the Fox equation.

In this respect, it is interesting to see if the composition dependence of the Tg of mixtures of **1** with **2** can be quantitatively fitted by relationships usually applied to polymers.

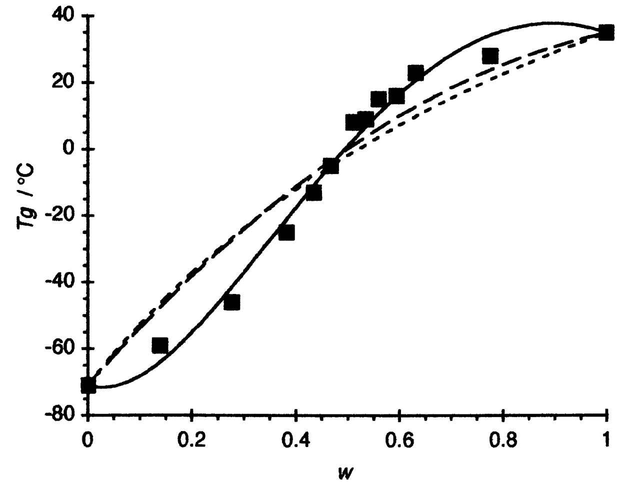


Fig. 5 Glass transition temperature (Tg) of mixtures of bispyridine **2** with bisphenol **1** *versus* weight fraction of bisphenol (w). Experimental data (■) and fits according to the Schneider (—), Kwei (- - -) and Gordon–Taylor (···) equations.

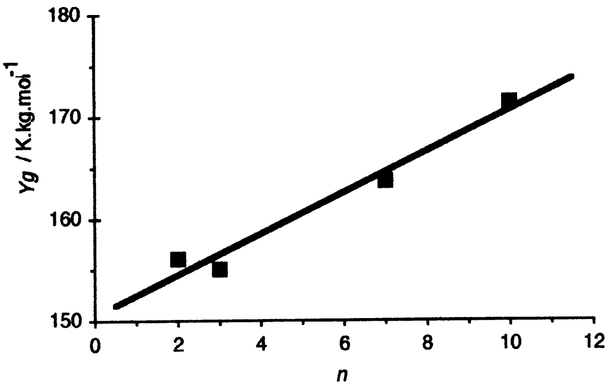


Fig. 6 Molar glass transition function (Yg) of bispyridines **5** to **8** *versus* number of methylene groups in the spacer (n).

Three such relationships were tested: the Gordon–Taylor equation

$$Tg = \frac{KwTg_1 + (1-w)Tg_2}{Kw + 1 - w} \quad (2)$$

where K is a constant,[13] the Kwei equation

$$Tg = \frac{KwTg_1 + (1-w)Tg_2}{Kw + 1 - w} + qw(1-w) \quad (3)$$

where K and q are constants,[14] and the Schneider equation

$$Tg = Tg_2 + (Tg_1 - Tg_2)((1+K_1)\phi - (K_1+K_2)\phi^2 + K_2\phi^3) \quad (4)$$

where

$$\phi = \frac{Kw}{1 - w + Kw} \quad (5)$$

and K, K_1 and K_2 are constants.[15,16] Best fits were obtained by least square analysis, and afforded the following values for parameters: $K = 1.9$ for eqn. (2), $K = 1$ and $q = 73$ K for eqn. (3) and $K = 1.4 \pm 0.3$, $K_1 = -1.3 \pm 0.5$ and $K_2 = -3.0 \pm 0.4$ for eqn. (4). Fig. 5 shows that in the case of eqns. (2) and (3), the fit is really poor. The change of concavity is not satisfactorily reproduced. Eqn. (4) affords a better fit, but this is partly due to the fact that three fitting parameters are allowed, which makes it easier to fit any data. Moreover, the fit is not perfect for extreme compositions. This lack of reliability of existing relationships, which are valid for polymers, shows that there is a need for relationships describing the Tg of low molecular weight compounds.

Influence of structure

In order to study systematically the influence of structure of the components on the Tg value of the mixture, several bispyridines were synthesized by esterification of 4-(3-hydroxypropyl)pyridine with diacid chlorides (Scheme 1). All the bispyridines synthesized afforded stable glasses when mixed with bisphenol A **1**. Firstly, aliphatic diacid chlorides were used to assess the influence of the length of the spacer between the two pyridine groups (bispyridines **5** to **8**). Table 1 shows that the longer the methylene spacer in the bispyridine, the lower the Tg of the equimolar mixture, which is expected because of the higher mobility resulting from the longer spacer. Here again, it is interesting to see if this effect is quantitatively similar in the case of low molecular weight compounds and polymers. Empirical relationships between structure and Tg are known in the case of polymers. For example, Van Krevelen defined the molar glass transition function Yg such that

$$Yg = Tg.M \quad (6)$$

where M is the molecular weight of the repeat unit.[17] He further showed that group contribution increments Yg_i can be computed from experimental Tg data, so that

$$Yg = \sum_i Yg_i \quad (7)$$

In homologous series of polymers (*i.e.* polyesters, polyamides), it has been shown that Yg is a linear function of the number of methylene groups in the repeat unit, with a slope of 2.7 to 4.3 K kg mol^{-1}. Consequently, Yg has been calculated for mixtures of **1** with bispyridines **5** to **8** and is represented in Fig. 6, *versus* the number of methylene groups in the spacer. As in the case of polymers, a linear relation is obtained, and the slope (2.0 K kg mol^{-1}) is close to usual polymer values. This result shows that an empirical approach to calculate the Tg of low molecular weight compounds can be used.

Secondly, bispyridines **9** to **11**, which have an aromatic spacer, are considered. Table 1 data show that mixtures of **1** with **9**, **10** or **11** have higher Tg values than mixtures of **1** with bispyridines **5** to **8**, due to the rigidity of the phenylene group. Moreover, a higher Tg is observed for the *para* isomer (**11**) than for the *ortho* (**9**) or *meta* (**10**) isomers, which is a known behavior in the case of polymers. However, the difference is quite small. It is interesting to see if it is possible to predict the difference between these Tg values using the empirical approach of Van Krevelen for the calculation of the Tg of polymers. Yg values are available for the *para* and *meta*-phenylene dicarboxylate moieties,[17] so that it is possible to calculate the difference of Tg between the equimolar mixture of **1** with **11** and **1** with **10** (ΔTg^{calc}) using eqns. (6) and (7). The calculated value ($\Delta Tg^{calc} = 9$ °C) is in very good agreement with the experimental value ($\Delta Tg^{exp} = 7$ °C).

Finally, a tetrapyridine (**12**) was synthesized to create a hydrogen bonded network with bisphenol A **1**, and thereby increase the Tg of the mixture. Such a reversible network based on a tetrapyridine has already been reported.[18] The mixture of **1** with **12** in an equimolar ratio of phenol and pyridine groups indeed affords the highest Tg of this homologous series (Table 1).

Table 1 Glass transition temperature of equimolar mixtures of bisphenol A **1** with bispyridines **5** to **11** and 2 : 1 mixture of **1** with **12**

Sample	Tg/°C	Sample	Tg/°C
1/5	−6	**1/9**	8
1/6	−14	**1/10**	5
1/7	−23	**1/11**	12
1/8	−27	**1/12**	31

Conclusion

Thus, even though compounds **1** and **2** are crystalline materials, it is possible to obtain a stable glass by mixing them together, because of intermolecular hydrogen bond formation between phenol and pyridine groups. The composition dependence of the Tg of the mixtures of **1** and **2** shows a very strong and positive deviation from the behavior of ideal copolymers or ideal polymer blends. This deviation is also due to hydrogen bonding. The strong influence of the structure of the low molecular weight compounds on the Tg of the mixture can be adequately described by empirical relationships, which are known in the field of polymers.

References

1 (*a*) M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120; (*b*) C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, **22**, 397; (*c*) J. C. MacDonald and G. M. Whitesides, *Chem. Rev.*, 1994, **94**, 2383.
2 (*a*) C. M. Paleos and D. Tsiourvas, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1696; (*b*) J. M. Lehn, in *Supramolecular Polymers*, ed.

A. Ciferri, Marcel Dekker Inc., New York, 2000, p. 615.; (*c*) T. Kato, *Struct. Bonding*, 2000, **96**, 95.

3 (*a*) I. Alig, D. Braun, R. Langendorf, H. O. Wirth, M. Voigt and J. H. Wendorff, *J. Mater. Chem.*, 1998, **8**, 847; (*b*) Y. Shirota, *J. Mater. Chem.*, 2000, **10**, 1.

4 T. Noda, H. Ogawa and Y. Shirota, *Adv. Mater.*, 1999, **11**, 283.

5 (*a*) M. Thelakkat and H. W. Schmidt, *Polym. Adv. Technol.*, 1998, **9**, 429; (*b*) M. Jandke, P. Strohriegl, S. Berleb, E. Werner and W. Brütting, *Macromolecules*, 1998, **31**, 6434; (*c*) D. F. O'Brien, P. E. Burrows, S. R. Forrest, B. E. Koene, D. E. Loy and M. E. Thompson, *Adv. Mater.*, 1998, **10**, 1108; (*d*) T. Noda and Y. Shirota, *J. Am. Chem. Soc.*, 1998, **120**, 9714; (*e*) T. Fuhrmann and T. Tsutsui, *Chem. Mater.*, 1999, **11**, 2226.

6 M. Brewis, G. J. Clarkson, A. M. Holder and N. B. McKeown, *J. Chem. Soc., Chem. Commun.*, 1998, 969.

7 N. Tamaoki, G. Kruk and H. Matsuda, *J. Mater. Chem.*, 1999, **9**, 2381.

8 (*a*) A. Higuchi, H. Inada, T. Kobata and Y. Shirota, *Adv. Mater.*, 1991, **3**, 549; (*b*) W. Ishikawa, H. Inada, H. Nakano and Y. Shirota, *J. Phys. D: Appl. Phys.*, 1993, **26**, B94; (*c*) Y. Shirota, K. Moriwaki, S. Yoshikawa, T. Ujike and H. Nakano, *J. Mater. Chem.*, 1998, **8**, 2579; (*d*) K. Moriwaki, M. Kusumoto, K. Akamatsu, H. Nakano and Y. Shirota, *J. Mater. Chem.*, 1998, **8**, 2671.

9 For studies of mixtures of hydrogen bonded solvents, see A. V. Lesikar, *J. Chem. Phys.*, 1975, **63**, 2297.

10 For studies of mixtures of carbohydrates, see P. D. Orford, R. Parker and S. G. Ring, *Carbohydr. Res.*, 1990, **196**, 11.

11 J. Almog, J. E. Baldwin, M. J. Crossley, J. F. Debernardis, R. L. Dyer, J. R. Huff and M. K. Peters, *Tetrahedron*, 1981, **37**, 3589.

12 M. Vivas de Meftahi and J. M. J. Fréchet, *Polymer*, 1988, **29**, 477.

13 M. Gordon and J. S. Taylor, *J. Appl. Chem.*, 1952, **2**, 493.

14 T. K. Kwei, *J. Polym. Sci., Polym. Lett. Ed.*, 1984, **22**, 307.

15 M. J. Brekner, H. A. Schneider and H. J. Cantow, *Polymer*, 1988, **29**, 78.

16 According to theory, the value of parameter K is supposed to be close to Tg_2/Tg_1,[15] but it can be treated as a fitting parameter to improve the quality of the fit. See A. Navia, R. M. Masegosa, M. G. Prolongo and A. Sanchis, *Polym. J.*, 1996, **28**, 217.

17 D. W. Van Krevelen, *Properties of Polymers*, 3rd Ed., Elsevier, Amsterdam, 1990.

18 K. N. Wiegel and A. C. Griffin, *Polym. Prep.*, 1999, **40**(2), 1136.