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Vitrigens

Part 2.†—Low molecular weight organic systems with high glass transition temperatures

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Low molecular weight organic materials characterized by a strong tendency towards glass formation and by glass transition temperatures around 100 °C are considered. They are constructed either as bulky odd-shaped molecules or as twin molecules where two bulky groups are linked *via* flexible or semi-flexible central groups. The synthesis of such materials, their structure – glass formation relationship and their miscibility with each other and with polymer matrices are described.

Low molecular weight organic compounds characterized by a reduced tendency towards crystallization and by glass transition temperatures well above room temperature are the exception rather than the rule.[1,2] The incorporation of small organic units into oligomer or polymer chain backbones or the attachment of such groups to polymer chain backbones, on the other hand, leads to systems which can be prepared in the majority of cases as amorphous glasses. The glass transition temperature is known to increase in both cases with increasing chain length and the tendency towards crystallization is reduced either for steric or for kinetic reasons.[3] This contribution is concerned with low molecular weight organic systems which exhibit glass transition temperatures in the range characteristic of polymers such as poly(methyl methacrylate) or polystyrene and which can be prepared in the fully noncrystalline state.

Low molecular weight organic materials with high glass transition temperatures may be of interest both from a scientific and application point of view.[4] With respect to fundamental science one wants to know the principal factors which control the position of the glass transition temperature. Such factors are, among other things, the molecular flexibility, the presence of steric hindrance and specific interactions such as the cohesion energy.

Low molecular weight glass forming systems may find many applications. It is well documented in the current literature that guest–host systems in which a glassy matrix serves as a host for functional molecules meet with a broad range of possible applications.[5–10] NLO-active systems for second harmonic generation (SHG) or for electro-optical modulation (Pockels effect) arise, for instance, if chromophores characterized by the absence of an inversion center are dissolved in a polymer matrix which is subsequently poled in a strong electric field.[5,6] Chromophores able to undergo a light-induced *trans–cis–trans* isomerization cycle have also been dispersed in glass forming matrices.[7,8] Such guest–host systems can be used for digital optical storage or holographic storage. A final example is organic light emitting diodes (LEDs) composed of chromophores dispersed in matrices having specific charge carrier transport properties.[9,10] The glassy matrix serves in all cases to allow film formation, and to reduce the tendency of the chromophores to crystallize. The glassy matrix may even provide special functions such as hole conduction as in the case of LEDs.

In the majority of cases the matrix is currently composed of polymers such as poly(methyl methacrylate) or polycarbonate. The use of polymer based guest–host systems has several advantages. A major advantage is that thin films with good dimensional and mechanical properties can easily be prepared by solution casting or spin-coating. A further advantage is that the systems may be optimized by choosing the host system from a large pool of commercially available and well characterized polymers.

Polymer based guest–host systems, on the other hand, have some serious disadvantages.

(i) The miscibility of the chromophores is limited in the majority of cases to a few percent or less. The major reason is that the entropy of mixing in such binary systems is strongly reduced due to the presence of the long chain molecules.[11] The long chain molecules, on the other hand, give rise to the high glass transition temperatures required for most applications. It is obvious that low molecular weight matrix systems with high glass transition temperatures offer advantages in terms of miscibility while keeping the glass transition temperature in the required range.

(ii) Polymer matrices have the tendency to age, a process which is accompanied by changes in the properties of the matrix. Chromophores dispersed in the polymer matrix are known to undergo relaxation processes which lead to a decay of their function.[5,6] It seems possible that low molecular weight vitrigens may be less sensitive in this respect.

The concept proposed in this paper is straightforward: in its first stage it envisages the replacement of the polymer matrix with a matrix composed of small molecules—which we will call in the following vitrigens—with the specific requirement that they have a high glass transition temperature of the order of 100 °C and above. In fact, it should even be possible to construct chromophores in such a way that they themselves act as vitrigens.

A second requirement is, of course, that the guest–host systems can be obtained as thin solid films by spin coating, for instance, and that the films possess good mechanical properties. The concept introduced above may thus have to be modified to take this requirement into account. The modification of the concept consists of replacing only a part of the polymer component by the low molecular weight vitrigen. A sufficient compatibility of chain molecules and low molecular weight glass formers has consequently to exist. The approaches taken by us to achieve this goal and the results obtained so far are described here.

Selection of appropriate chemical structures

Considerations based on incremental methods[12] or on free volume concepts[13] suggest that bulky molecular systems and

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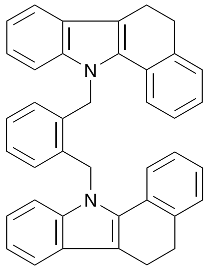
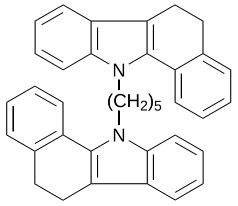
systems with strong attractive interactions should exhibit a tendency towards high glass transition temperatures. The requirement is, on the other hand, that the molecular system should have a weak tendency towards crystallization despite the strong intermolecular attraction. Molecules with irregular shapes and molecules able to exist in a large number of different conformations in the fluid state at nearly identical energy should possess a weakened tendency towards crystallization, mainly for kinetic reasons.

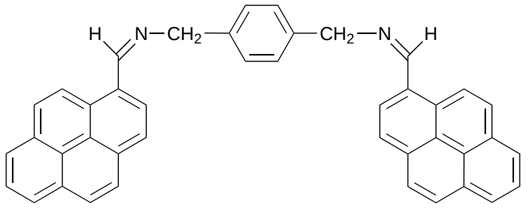
Based on such considerations we selected the following model systems.

(i) Twin molecules (*e.g.* BECADHOX) where two identical bulky groups are linked *via* a central group (symmetric twins). The central links can be selected to be flexible or semi-flexible. These types of molecules allow one to easily introduce a broad range of further modifications such as a variation of the length, flexibility and shape of the central link.

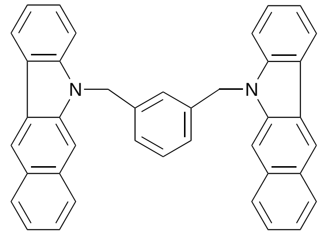

BECADHOX



BECADHC5

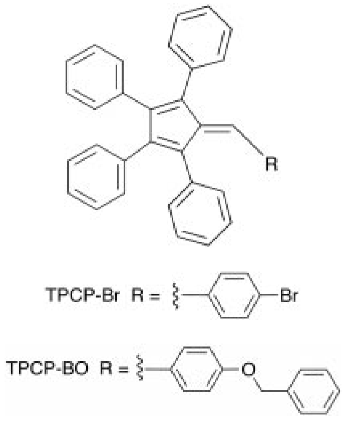


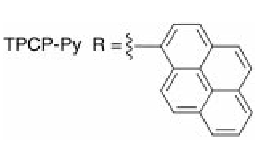
PYDAPX



BCX

(ii) A second approach was based on bulky odd-shaped molecules which allowed the introduction of the functional groups, *i.e.* chromophores directly into the glass forming compounds. Fulvenes were considered in particular (*e.g.* TPCP derivatives). Details of the synthesis and the properties will be given below.





Synthesis

^{1}H NMR spectra were obtained on a Bruker WM-300 instrument and chemical shifts are given in ppm downfield from Me_4Si. Mass spectra were obtained on a Varian 311A instrument in the field-desorption mode. Differential scanning calorimetry measurements were carried out on a Du Pont 912 or a Perkin-Elmer DSC 7 instrument. Samples of 5–10 mg in solid form were put in aluminium pans and heated at a scan rate of 10 or 20 °C min^{-1} under a nitrogen flow. The melting points were measured at the first heating. Indium metal was used as standard. After melting, the samples were rapidly cooled to room temperature. The resulting glasses were heated under the same conditions again to measure the glass transition. Elemental analyses were performed using a Perkin-Elmer 240 elemental analyser.

1,4-Bis(pyren-1-ylmethylidene)aminomethylbenzene (PYDAPX)

In a 500 ml three-necked round-bottomed flask equipped with a water separator (Dean–Stark), reflux condenser and a dropping funnel were placed 2.30 g (10 mmol) of pyrene-1-carbaldehyde dissolved in 100 ml of toluene. The reaction mixture was heated to reflux followed by addition of a solution of 0.68 g (5 mmol) of 1,4-bis(aminomethyl)benzene dissolved in 50 ml of toluene over a period of 1 h. Then the solution was refluxed for 3 h. After cooling to room temp. the precipitated crystals were filtered and the crude product was recrystallized from toluene and dried *in vacuo*. Yield: 2.10 g (75%), mp 213 °C, glass transition (T_g) 95 °C. δ_H (300 MHz, [$^2H_8$]THF) 5.04 (s, 4H, N-CH_2-), 7.49 (s, 4H, Ar-H), 8.00–8.26 (m, 14H, Ar-H), 8.63–8.66 (d, 2H, Ar-H), 9.20–9.23 (d, 2H, Ar-H), 9.49 (s, 2H, C-H). Calc. for $C_{42}H_{28}N_2$ (M 560.7) C, 89.97; H, 5.03; N, 5.00. Found: C, 90.05; H, 5.04; N, 4.91%. MS (*m*/*z*): 561 (M$^+$).

1,3-Bis(benzo[*b*]carbazol-9-ylmethyl)benzene (BCX)

In a 100 ml three-necked, round-bottomed flask equipped with a reflux condenser and a dropping funnel were placed 4.35 g (20 mmol) of benzo[*b*]carbazole (Rütgerswerke AG) in 30 ml of dimethyl sulfoxide. Under nitrogen and with stirring 1.68 g (30 mmol) of potassium hydroxide were added. The suspension was stirred about 1 h at 50 °C. Then the reaction mixture was cooled to room temp. and a solution of 1.75 g (10 mmol) of α,α′-dichloro-*m*-xylene dissolved in 20 ml of dimethyl sulfoxide was added slowly. The solution was warmed to 90 °C for 1 h. Then 200 ml of water were added and the crude product was separated. Then the crude product was dissolved in hot chloroform and dropped in an excess of methanol (10 : 1 v/v). After separating the product was filtered and dried *in vacuo*. Yield: 4.9 g (91%), mp 247 °C, T_g 90 °C. Calc. for $C_{40}H_{28}N_2$ (M 536.7), C, 89.52; H, 5.26; N, 5.22. Found: C, 89.56; H, 5.40; N, 5.04%. MS (*m*/*z*): 536 (M$^+$).

3,4-Dihydrobenzo[*a*]carbazole derivatives

1,5-Bis[(3,4-dihydrobenzo[*a*]carbazol-9-yl]pentane (BECADHC5). In a 100 ml three-necked round-bottomed flask equipped with a reflux condenser and a dropping funnel were placed 2.19 g (10 mmol) of 3,4-dihydrobenzo[*a*]carbazole (Rütgerswerke AG) dissolved in 30 ml of 1-methylpyrrolidin-2-one under a stream of nitrogen. Then the mixture was warmed at 80 °C and 0.70 g (12.5 mmol) of potassium hydroxide was added; the colour changed from pale to yellow. After 4 h 1.15 g (5 mmol) of 1,5-dibromopentane dissolved in 20 ml of 1-methylpyrrolidin-2-one were added during 30 min. The reaction was stopped after 10 h. The solution was then filtered and poured in an excess of methanol (10 : 1 v/v). The separated white crystals were filtered and dried *in vacuo*. Yield: 1.77 g (70%), mp 149 °C, T_g 40 °C. δ_H (300 MHz, $CDCl_3$) 1.37–1.45 (m, 2H, -CH_2-), 1.88–1.98 (m, 4H, -CH_2-), 2.85–2.98 (m, 8H, -CH_2-), 4.32–4.37 (t, 4H, -CH_2-N), 7.09–7.32 (m, 12H, Ar-H), 7.46–7.49 (d, 2H, Ar-H), 7.55–7.57 (d, 2H, Ar-H). Calc. for $C_{37}H_{34}N_2$ (M 506.7), C, 87.71; H, 6.76; N, 5.53. Found: C, 87.60; H, 6.92; N, 5.48%. MS (*m*/*z*): 506 (M^+).

1,2-Bis[(3,4-dihydrobenzo[*a*]carbazol-9-yl)methyl]benzene (BECADHOX). This was synthesized analogously to BECADHC5 from 2.19 g (10 mmol) of 3,4-dihydrobenzo[*a*] carbazole and 0.88 g (5 mmol) of α,α′-dichloro-*o*-xylene. Yield: 1.76 g (65%), mp 245 °C, T_g 112 °C. δ_H (300 MHz, $CDCl_3$) 2.96 (m, 8H, -CH_2-), 5.43 (s, 4H, CH_2-N), 6.99–7.03 (m, 2H, Ar-H), 7.10–7.22 (m, 14H, Ar-H), 7.30–7.32 (m, 2H, Ar-H), 7.59–7.61 (d, 2H, Ar-H). Calc. for $C_{40}H_{32}N_2$ (M 540.7) C, 88.85; H, 5.97; N, 5.18. Found C, 88.81; H, 6.06; N, 5.13%.

Fulvenes

6-(4-Benzyloxyphenyl)-1,2,3,4-tetraphenylfulvene (TPCP-BO). In a three-necked round-bottomed flask equipped with a reflux condenser and a dropping funnel were placed 1.85 g (5 mmol) of 1,2,3,4-tetraphenylcyclopenta-1,3-diene (Aldrich) and 3.18 g (15 mmol) of 4-benzyloxybenzaldehyde dissolved in 45 ml of absolute methanol. The reaction mixture was heated to reflux followed by addition of 90 ml of sodium methoxide (4 wt% in methanol) during 30 min. After refluxing for 18 h the mixture was cooled to room temperature. The precipitated red crystals were filtered by suction and washed three times with methanol before drying *in vacuo* at 40 °C for 24 h. Yield: 0.73 g (26%), mp 169 °C, T_g 73 °C. δ_H (300 MHz, $CDCl_3$) 4.96 (s, 2H, -CH_2-), 6.48–7.61 (m, 30H, Ar-H and C-H). Calc. for $C_{43}H_{32}O$ (M 564.7), C, 91.46; H, 5.71. Found C, 91.21; H, 5.58%. MS (*m*/*z*): 564 (M^+).

6-(4-Bromophenyl)-1,2,3,4-tetraphenylfulvene (TPCP-BR). This was synthesized analogously to TPCP-BO from 0.93 g (2.5 mmol) of 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1.85 g (10 mmol) of 4-bromobenzaldehyde in 30 ml of absolute methanol and 45 ml (*ca.* 28 mmol) of sodium methoxide (4 wt% in methanol). Reaction time: 6 h, yield: 1.26 g (94%), mp 187 °C, T_g 84 °C. δ_H (300 MHz, $CDCl_3$) 6.76–7.33 (m, 25H, Ar-H and C-H). Calc. for $C_{36}H_{25}Br$ (M 537.5), C, 80.45; H, 4.69. Found: C, 80.05; H, 4.51%. MS (*m*/*z*): 536/538 (M^+).

1,2,3,4-Tetraphenyl-6-(pyren-1-yl)fulvene (TPCP-PY). This was synthesized analogously to TPCP-BO using 1.85 g (5 mmol) of 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 2.30 g (10 mmol) of pyrene-1-carbaldehyde in 60 ml absolute methanol and 90 ml (*ca.* 56 mmol) of sodium methoxide (4 wt% in methanol). Reaction time: 10 h, yield: 1.33 g (46%), mp 282 °C, T_g 118 °C. δ_H (300 MHz, $CDCl_3$) 6.35–8.22 (m, 30H, Ar-H and C-H). Calc. for $C_{46}H_{30}O$ (M 582.7), C, 94.81; H, 5.19. Found: C, 94.97; H, 5.16%. MS (*m*/*z*): 582 (M^+).

Experimental techniques

X-Ray studies

The structure of the bulk solid state of the vitrigens and of the blends with polymers was analysed at room temperature in the glassy state employing a wide angle X-ray goniometer (Siemens D 5000) in the reflection mode.

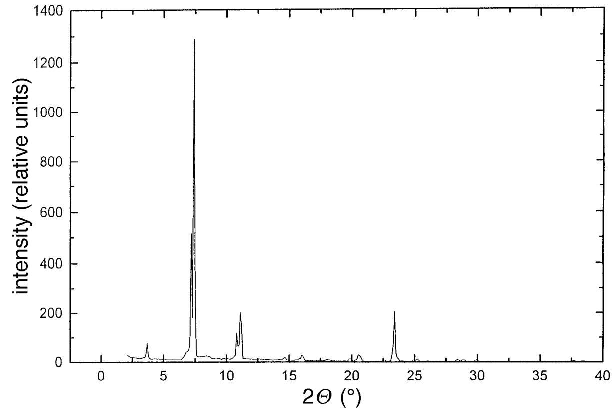


Fig. 1 X-Ray diagram of PYDAPX as obtained from synthesis

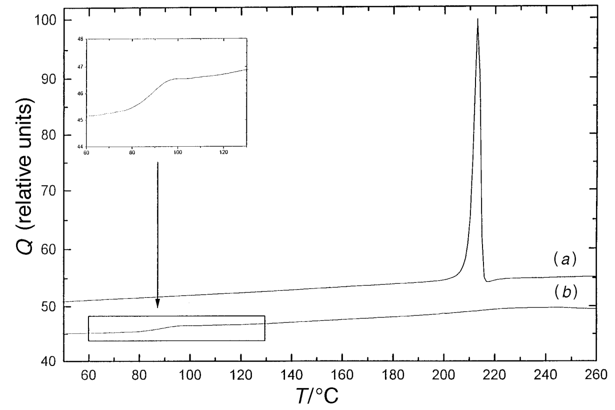


Fig. 2 DSC diagram of (*a*) the melting endotherm of PYDAPX and (*b*) the melt quenched PYDAPX

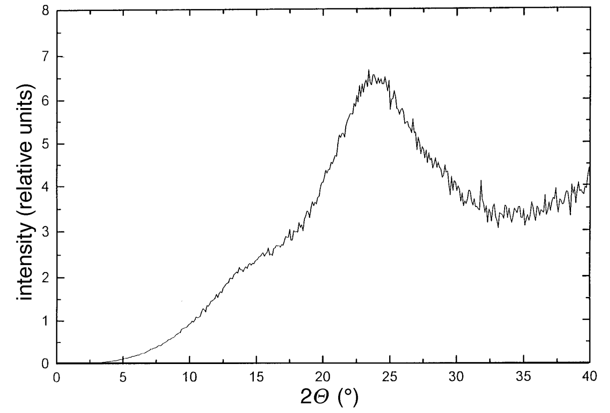


Fig. 3 X-Ray diagram of the melt quenched PYDAPX

Glass formation of the low molecular weight systems

The tendency towards glass formation was analysed using calorimetric and X-ray scattering investigations. The results obtained will be discussed predominantly using the vitrigen PYDAPX as an example. The powder obtained from the synthesis was crystalline as is apparent from the X-ray diagram (Fig. 1).

The diagram is characterized by the absence of any trace of an amorphous halo, the occurrence of which would indicate a partially crystalline state. The reflections are narrow even for higher order reflections. This can be taken as an indication of rather perfect and large crystals. Based on the location of the reflections we tentatively assign this scattering diagram to an orthorhombic unit cell with the cell parameters $a = 23.6$

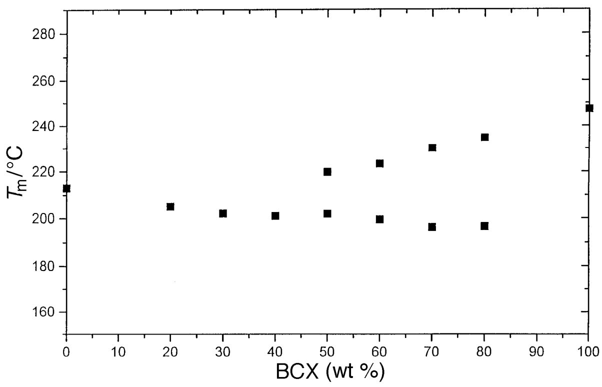


Fig. 4 Melting points of binary mixtures of PYDAPX and BCX

Table 1 Melting temperatures (T_m), glass transition temperatures (T_g), crystallization temperatures (T_c) and decomposition temperatures (T_z)

substance	T_g/°C	T_c/°C	T_m/°C	T_z/°C
PYDAPX	95	—	213	280
BCX	90	—	247	270
BECADHOX	112	208	245	300
BECADHC5	40	108	149	270
TPCP-BO	73	—	169	290
TPCP-BR	84	—	187	225
TPCP-PY	118	191	282	310

$b = 8.0$ and $c = 3.8$ Å. The crystallographic density amounts to 1.3 g cm^{-3} which agrees approximately with the pyknometer result (1.35 g cm^{3}).

Fig. 2 displays in the the upper curve (1) the melting endotherm of this compound. The melting peak is narrow and it is located at 216 °C; the enthalpy of fusion amounts to 65.1 kJ mol^{-1}. Such a high value of the enthalpy of fusion is in agreement with the presence of a perfect crystalline state of the compound as found by X-ray analysis.

The melt may be quenched into the glass state at moderate cooling rates of the order of 1–10 K min^{-1}. The X-ray diagram obtained from the quenched state (Fig. 3) is characterized by a broad halo showing two maxima. Such a scattering diagram is characteristic of a truly amorphous state: the two maxima reflect the packing of the anisometric building blocks of the molecule.

The DSC heating curve of the quenched state reveals (Fig. 2, lower curve) a stepwise increase of the specific heat which is of the order of 0.18 J g^{-1} K^{-1} which is in the range also typically observed for polymer systems.[14] The glass transition temperature occurs at 95 °C and is thus in the temperature range required for the applications described above.

The results described so far for the model system PYDAPX are characteristic of all the twin systems and the odd-shaped ones. Table 1 displays the melting temperatures (T_m), the glass transition temperatures (T_g), the crystallization temperatures (T_c) and the decomposition temperatures (T_z). It is apparent that glass transition temperatures up to 118 °C were obtained. Of particular interest is the case of the fulvenes. These chromophores form a glassy state at elevated temperatures so that they may be directly used to produce thin solid functional films.

The conclusions which can be drawn from the results reported so far are that the compounds under investigation can be transferred into the glassy state using non-exotic (*i.e.* moderate cooling) conditions and that the glass transition temperatures approach the temperature range required for application in guest–host systems (>100 °C). This even holds for chromophores such as the fulvenes studied here.

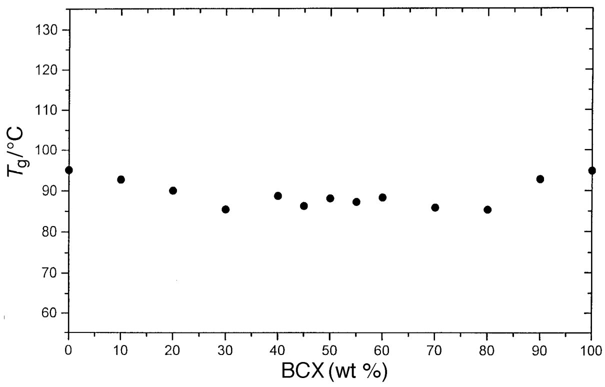


Fig. 5 Variation of the glass transition temperatures of binary blends of PYDAPX and BCX with composition

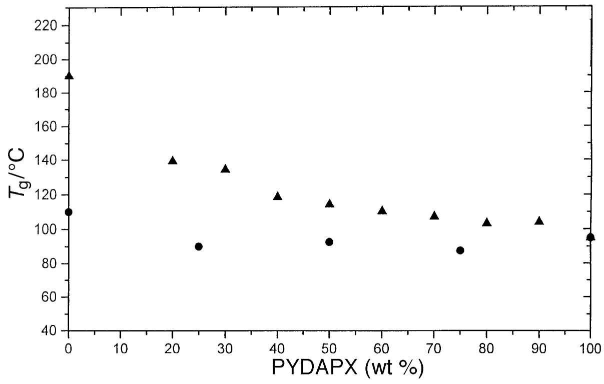


Fig. 6 Variation of the glass transition temperatures of binary blends of (▲) PYDAPX and Durel and (●) PYDAPX and PMMA with composition

Glass formation of mixtures of the low molecular weight systems

It can be expected that the tendency towards crystallization and that the melting points of the systems are reduced in binary mixtures. The experimental results agree with such expectations. The mixing of two vitrigens leads to a strong decrease of the melting temperature at intermediate concentrations. This is evident from the results of the calorimetric analysis shown in Fig. 4 for the particular case of mixtures of the compounds PYDAPX and BCX.

The diagram evidently shows eutectic behavior as expected for the case of an immiscible crystalline state and a miscible molten state. The melting temperature can be reduced to about 470 K in the eutectic mixture. We find only one glass transition temperature of the melt-quenched material which varies very smoothly with the composition of the melt (Fig. 5).

Table 2 Characteristic parameters of the polymers used for the blends

polymer	short name	producer	M_w	M_n	ρ/g cm^{-3}	T_g/°C
poly(ethyl acrylate)	PEA	Röhm		17000	1.12	−15
poly(methyl meth-acrylate)	PMMA	Polysciences, Inc.	100000	53000	1.15	110
poly(vinyl acetate)	PVAc	Polysciences, Inc.	500000		1.05	30
polyarylate	PAR/Durel	Hoechst	54500	27600	1.22	190

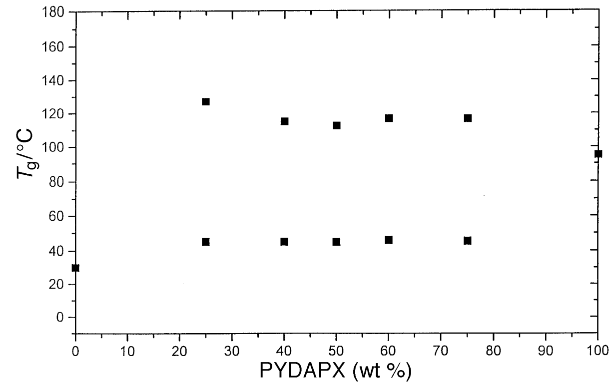
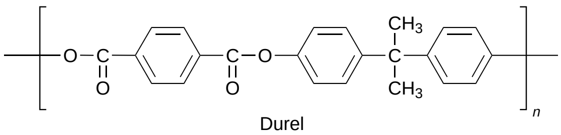


Fig. 7 Variation of the glass transition temperatures of binary blends of PYDAPX and PVAc with composition

This is not surprising in view of the fact that the two glass transition temperatures are about equal. The diagram shown in Fig. 5 does thus not allow conclusions to be drawn on the state of mixing of the two components in the glassy state. Yet the eutectic behavior described above strongly suggests miscibility in the fluid and thus also in the glassy state. The observations that the glassy films are transparent and reveal no inhomogeneity under the microscope point in the same direction. Similar results were obtained for other binary blends of vitrigens.

Glass formation of mixtures of the low molecular weight systems with amorphous polymers

Information on the miscibility of the low molecular weight compounds with the amorphous poly(methyl methacrylate) (PMMA), Durel (a polyarylate), and poly(vinyl acetate) (PVAc) were obtained using calorimetry and X-ray diffraction. Characteristic parameters of the polymers are given in Table 2.



Durel

First, both the X-ray analysis and the calorimetric studies reveal that the low molecular weight compounds dispersed in the polymer do not crystallize on cooling. The variation of the glass transition with composition indicates miscibility at all concentrations in the case of mixtures with Durel (Fig. 6, upper curve).

The temperature at which a stepwise increase of the specific heat is observed in the blends varies continuously with the composition. The nonlinearity of the curve connecting the glass transition temperatures is not unusual. Differences in the magnitude of the stepwise increase of the specific heat connected with the glass transition of the two components are probably the origin.[15] A similar observation was made for mixtures with PMMA (Fig. 6, lower curve).

The closeness of the glass transition temperatures of PMMA and of the low molecular weight compound, however, makes it impossible to conclude that the glassy state is homogeneous. The optical clarity however points in this direction.

Finally we consider the case of blends with PVAc (Fig. 7). We observe two well separated glass transition temperatures: the two compounds are not miscible. The conclusion is thus that homogeneous mixtures of polymer and low molecular weight components with elevated glass transition temperatures can be achieved in certain cases whereas the entropic driving force towards mixing is not strong enough in other cases.

Conclusions

Low molecular weight organic materials able to form the glassy state and characterized by glass transition temperatures well above room temperature—vitrigens—can be constructed on the basis of twin molecules and bulky irregularly-shaped molecules. The building blocks can be selected to be chromophores. Thin films with good optical properties can be prepared by spin-coating either using mixtures with amorphous polymers or using the pure vitrigens.

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