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The use of molecular recognition to obtain selective blending in polymer systems

J.M.G. Cowie*, C. Love

Department of Chemistry, Heriot-Watt University, Riccarton Campus, Edinburgh EH14 4AS, UK

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Abstract

A series of copolymers were prepared in which specific hydrogen bonding sites were incorporated that were either the pyrimidine–purine base pairings found in DNA or analogues of these. Copolymers of poly(methylacrylate-*stat*-maleimide), MA/MI, were blended with samples of copolymers poly(styrene-*stat*-7-[2-methacryloyloxy] ethyladenine), S/MAAd, and poly(methyl methacrylate-*stat*-7-[2-methacryloyloxy]ethyladenine), MMA/MAAd, and found to form miscible blends when the composition of the copolymers contained $\geq$15 mol% of the hydrogen bonding units, MI and MAAd. These form triple hydrogen bonded structures and promote stable one phase blend formation.

However, it was found that if S/MAAd was blended with copolymers of poly(methylacrylate-*stat*-vinyl cytosine) the blends were immiscible over the whole range of compositions studies. This was attributed to the fact that cytosine and adenine do not form stable hydrogen bonded combinations in nature and will selectively reject each other as complementary hydrogen bonding pairs. This shows that in principle the use of such units in synthetic polymer systems could allow selective blending and the formation of controlled structures.
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1. Introduction

The formation of single phase, miscible, polymer blends usually requires the presence of favourable inter-component interactions that contribute a negative enthalpy of mixing (ΔH^m), contribution to the free energy of mixing (ΔG^m). While some polymers can have, either or both, donor (D) and acceptor (A) groups inherent in their chemical structures, others may have to be modified by introducing suitable D or A sites into the chain. There are several ways [1] in which this can be achieved and secondary bonding interactions, such as coulombic attractions [2], ion–dipole interactions [3–5], charge-transfer complex formation [6,7] and hydrogen bonding [8–11] have all been used to good effect.

The amount of modification that is necessary will depend on how immiscible are the starting components and the relative flexibilities of the chains. Thus, if the components have widely differing solubility parameters (δp) (if we use this as a rough guide to miscibility) they can be regarded as immiscible and will require a larger number of successful D–A interactions to bridge the energy gap ($\Delta\delta$) than in a less immiscible system where $\Delta\delta p$ is smaller. Also as successful secondary bonding interactions usually require the D and A sites to be close enough for the bonds to form, not all of the sites in a polymer chain will be involved in bonding as chain flexibilities may affect the accessibility of the D/A sites in the chain.

In most cases reported, a D site does not necessarily discriminate amongst the available A sites even though the A sites may differ in chemical structure, and vice versa. Exceptions to this are found in charge-transfer complex formations [6,7,12–14] and the use of structures analogous to DNA where the complementary base pairing is highly selective: [11,15–18]. While the lack of discrimination between D and A sites is useful in promoting miscibility in polymer blends the possibility of very selective D–A pair interactions presents an opportunity to form more precisely defined multi-component systems. The model observed in nature is of course the pyrimidine–purine base pairings in DNA which are very specific, and although mistakes in pairing the wrong couple are possible [19] they are rare and consequently one expects selective bonding of guanine with cytosine and adenine with thymine (or uracil) to occur exclusively.

The groups that are used to achieve this site-specific secondary bonding need not necessarily be those found in

* Corresponding author. Tel.: +44-131-451-3160; fax: +44-131-451-3180.

E-mail address: j.m.g.cowie@hw.ac.uk (J.M.G. Cowie).

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DNA, as structurally similar units can be used with equal effect. Lehn and coworkers [15,16] prepared both telechelic structures from tartaric acid derivatives and dianhydride units terminated with uracil or 2,6-diacyl amino pyridine groups that formed end to end associated chains through triple hydrogen bonding of the DAD to ADA type bonding. We have used a similar pairing to promote miscibility in polymer blends in which a polymer containing maleimide (MI), a triple bonding (ADA) site, interacts with another polymer incorporating 2,4-diamino-1,3,5-triazine units that are sterically acceptable, complementary, (DAD) sites [11].

In this paper, we have tested the principle further, by studying whether polymers containing units such as MI will interact with polymers containing the complementary adenine unit, but reject a polymer with the non-matching cytosine incorporated in the chain.

2. Experimental section

2.1. Reagents

The monomers MI, methyl acrylate (MA), methylmethacrylate (MMA) and styrene (S) were purchased from Aldrich and purified before use.

The other monomers used to prepare the copolymers were synthesised as described below and all the reagents used were also purchased from Aldrich unless otherwise specified.

2.2. Monomer synthesis

2.2.1. Synthesis of 7-(2-methacryloyloxy)ethyl adenine (MAAd)

A two stage synthesis was used to prepare this monomer.

2-Bromoethyl methacrylate. Methacrylic acid (43.8 g, 0.5 mole), 2-bromoethanol (93.77 g, 0.75 mole)and *p*-toluene sulphonic acid (6.18 g) in toluene (30 ml) were refluxed until the theoretical amount of water had been collected in a Dean–Stark trap (approximately 3 h). On cooling, the solution was washed with 20% potassium hydroxide and with water and dried over magnesium sulphate. After filtration and removal of solvent, the product was distilled under reduced pressure (56°C, 0.5 mbar).

Yield = 66.9 g (69.5%). IR (thin film) ν_{max} (cm^{-1}): 1723 C=O stretch; 1638 C=C; 1158 C–0; 650 C–Br. ^{1}H NMR ($CDC1_3$) δ (ppm): 1.9 (s, 3H) CH_3; 3.5 (t, 2H) CH_2Br; 4.4 (t, 2) CH_2O; 5.6 (m, 1H) vinyl H; 6.15 (m, 1H) vinyl H. ^{13}C NMR (DEPT) ($CDC1_3$) δ (ppm): 18.1 CH_3; 28.6 CH_2Br; 63.9 CH_2O; 126.1 CH_2 alkene; 135.8 quaternary C alkene; 166.7 quaternary C ester.

7-(2-Methacryloyloxy)ethyl adenine. This synthesis followed the method used by Akashi et al. [20].

A suspension of the sodium salt of adenine was prepared in dry dimethylformamide (250 ml) from sodium hydride (0.48, 0.02 mole) and adenine (2.7 g, 0.02 mole) by stirring at 60° for 2 h. The suspension was cooled to 40°C and 2-bromoethyl methacrylate (5.8 g, 0.03 mole) was added dropwise. Stirring was continued for 24 h. After removal of the solvent, the product was recrystallised from ethanol.

Yield = 3.01 g (61%). IR (KBr disc) ν_{max} (cm^{-1}): 3417, 3353 NH_2 stretch; 1714 C=O stretch; 1637 C=C; 1603 NH_2 bend; 1191 C–O. ^{1}H NMR (d_6-DMSO) δ (ppm): 1.75 (s, 3H) CH_3; 4.45 (s, 4H) O–CH_2CH_2–N; 5.6, 5.9 (m, 2H) vinyl CH_2; 7.25 (s, 2H) NH_2; 8.15 (2 × s, 2H) Ar–H. ^{13}C NMR (DEPT) (d_6-DMSO) (ppm): 17.7 CH_3; 41.9 N–CH_2; 62.5 O–CH_2; 118.6 C=C quaternary; 125.9 CH_2; 135.4 N=C quaternary; 140.9 CH alkene; 149.6 C=C quaternary; 152.4 CH alkene; 155.9 C=C quaternary; 166.0 C=O.

2.2.2. Synthesis of l-vinylcytosine (VCy)

1-(2′-Hydroxyethyl)-cytosine. A solution of cytosine (1.111 g, 0.01 mole) and ethylene carbonate (1 g, 0.01 mole) in distilled dimethylformamide (60 ml) containing a trace of sodium hydroxide was boiled for 10.5 h. The dark orange solution contained solid material which was filtered off. The solid was washed in 7 ml of ethanol to give the product.

Yield = 0.715 g (45%). IR (thin film) ν_{max} (cm^{-1}): 3475 OH stretch; 3345, 3204 NH_2; 2957, 2887 C–H stretch; 1654 amide C=O; 1609 NH_2 bend. ^{1}H NMR (d_6-DMSO δ (ppm): 3.5 (t, 2H) CH_2; 3.7 (t, 2H) CH_2; 5.0 (s, 1H) OH; 5.65 (d, 1H) vinyl C–H *trans* to NCH_2CH_2OH; 7.1 (2 × s, 2H) NH_2; 7.5 (d, 1H) vinyl C–H *gem* to NCH_2CH_2OH. ^{13}C NMR (DEPT) (d_6-DMSO) δ (ppm): 42.2 CH_2; 50.5 CH_2; 93.6 CH vinyl; 147.8 quaternary C–NH_2; 150.4 CH vinyl; 160.4 quaternary C=O.*1-(2′Chloroethyl) cystosine.* 1-(2prime;-Hydroxyethyl)-cytosine (0.65 g, 4.2 mmole) was suspended in 20 ml of anhydrous dioxane to which was added ten drops of pyridine. Thionyl chloride (1.50 g, 12.6 mmole) dissolved in 25 ml anhydrous dioxane was added dropwise to the suspension. Yellow sticky material formed. The reaction was refluxed for 50 min and stirred overnight. The solvent was removed under reduced pressure to give a pale pink solid, which was recrystallised from ethanol.

Yield = 0.405 g (57%). IR (thin film) ν_{max} (cm^{-1}): 3316, 3077 NH_2 stretch; 1676 amide C=O; 1611 NH_2 bend; 616 C–C1. ^{1}H NMR (d_6-DMSO) δ (ppm): 3.9 (t, 2H) CH_2; 4.1 (t, 2H) CH_2; 6.2 (d, 1H) vinyl CH; 8.1 (d, 2H) vinyl CH; 8.9 (s, 1H) NH; 10.05 (s, 1H) NH. The shift in the NH_2 position is due to the level of water in the DMSO. No OH resonance is observed and the shift in the ethyl CH_2 is consistent with the conversion of OH to Cl. ^{13}C NMR (DEPT) (d_6-DMSO) δ (ppm): 42.2 CH_2; 50.5 CH_2; 93.6 CH vinyl; 147.8 quaternary C–NH_2; 150.4 CH vinyl; 160.4 quaternary C=O.

l-Vinylcytosine. To 1-(2′-Chloroethyl)cytosine (10.3 g) suspended in 850 ml anhydrous dioxane was added to a solution of sodium methoxide (30.2 g) in methanol (100 ml). The mixture was stirred at room temperature for seven days. Water was added until solution resulted. The solution was treated with Amberlite IR-120 (H) resin, which was filtered off. The resin was treated with a 50:50 solution of water and pyridine to remove the product. The solvent

was removed to leave an orange solid. Boiling water was added and the solid impurity filtered off. Further purification was carried out by flash chromatography ($CHCl_3$ (95%), MeOH (5%)) to give 93% pure Vcy. Recrystallisation from $CHC1_3$/MeOH gave yellow crystals of 96% pure Vcy (impurity CyEtCl). The impurity will not interfere with a polymerisation reaction, therefore the product will be used as is.

Yield = 1.693g (20%). IR (thin film) ν_{max} (cm^{-1}): 3323, 3176 NH_2 stretch; 1647 amide C=O; 1609 NH_2 bend. ^1H NMR (d_6-DMSO) δ (ppm): 4.9 (dd38, 1H) vinyl *gem*; 5.35 (dd, 1H) vinyl *gem*; 6.0 (d, 1H) vinyl (cytosine); 7.1 (dd, 1H) vinyl; 8.1(d, 2H) vinyl (cytosine) +NH; 8.7 (s, 1H) NH. ^{13}C NMR (DEPT) (d_6-DMSO) δ (ppm): 95.9 CH vinyl; 99.6 CH_2 vinyl; 132.0 CH cytosine vinyl; 140.1 CH cytosine vinyl; 154.3 quaternary C–NH_2; 166.0 quaternary C=O.

2.3. Copolymer synthesis

2.3.1. Copolymerisation of methyl acrylate (MA) and maleimide

The copolymerisation of MA and MI was carried out in a 4:1 molar ratio of dry THF with 0.25 mol% α,α'-azobisisobutyronitrile (AIBN) as initiator. The vessel was freeze/pump/thawed three times prior to sealing under vacuum and placing in a 60°C water bath for 30 min. The copolymers were obtained as white solids after precipitation in methanol and reprecipitation from THF into methanol.

The polymers with the following mol% of MI in the feed were prepared 6, 13, 20, 30, 40, 50, 60, 70, and 80.

2.3.2. Copolymerisation of styrene with 7-(2-methacryloyloxy)ethyl adenine

The copolymerisation of styrene with MAAd was carried out in *N*-methyl pyrrolidinone (NMP) with 0.2 mol% AIBN as the initiator. The solubility of MAAd in NMP required the level of solvent used to be increased with increasing feed of MAAd (2.8 ml for poly(styrene) to 8 ml for poly(MAAd). The polymerisations were carried out at 60°C.

Excess NMP was removed under reduced pressure and the polymers precipitated into a ten-fold excess of methanol. The exception to this was poly(MAAd) which was precipitated into water and then from dimethylsulphoxide into ethanol. The copolymers and homopolymers were purified by either reprecipitation or by stirring overnight in a suitable non-solvent.

The absence of NMP was confirmed by NMR. The infrared and NMR spectra are similar for all the copolymers. The compositions of the copolymers were determined from ^1H NMR spectroscopy from the ratio of the integrals of the peak for one of the purine protons in the MAAd (δ 8.3 ppm) and the aromatic protons in the styrene unit, which overlapped with the second purine proton (δ about 7 ppm).

2.3.3. Copolymerisation of methylacrylate with vinyl cytosine

The copolymerisation of methyl acrylate and vinyl cytosine was carried out in NMP as solvent containing 0.2 mol% AIBN. The reaction was carried out at 60°C for, on average, 20 h and the copolymers formed were isolated by precipitation into acetone. Products were purified by stirring overnight in water followed by drying in a vacuum oven. The absence of solvent was confirmed by NMR.

2.3.4. Copolymerisation of methyl methacrylate and 7-(2-methacryloyloxy)ethyl adenine

Copolymers of MMA and MAAd were prepared as above except that the reaction time was on average 3 h and copolymers were isolated by precipitation into a ten-fold excess of methanol. Again products were purified by stirring overnight in water and then vacuum dried.

2.4. Copolymer characterisation

Copolymer compositions were determined using both NMR and elemental analysis. A Bruker AC 200 was used to measure the ^1H NMR using deuterated DMSO as solvent ^{13}C spectra were determined using a 50 MHz Bruker DP X400 instrument. Infra-red spectra were measured using a Perkin–Elmer 1720X FT-IR. Glass transition temperatures (T_g) were obtained using a Perkin–Elmer DSC4 or a Mettler FP90 and were taken at the temperature of the onset of the base line shift.

2.5. Copolymer blend preparation

Copolymer blends were prepared by coprecipitation of a solution of the copolymers into a non-solvent. The common solvents used were NMP or $CHCI_3$ and the precipitants were methanol or acetone. Compositions of the blends were limited to 50:50 (mol%).

3. Results and discussion

Several copolymers were prepared for blending that have not been reported previously and some basic characteristics of these are now described.

3.1. Poly(methyl acrylate-stat-maleimide), MA/MI

A series of copolymers were prepared using: (1) methylacrylate; and (2) MI. The copolymerisation reactions were terminated at approximately 10% conversion to minimise composition drift and the compositions were determined both by elemental analysis and ^1H NMR. In the latter case the composition for each sample was calculated by comparing the integrals for the peak associated with the imide proton in the MI unit ($\delta = 11.25$) with those for the ethoxy methyl protons in the methyl acrylate unit ($\delta = 3.6$). The results from the two methods agree to within 2 mol% and are shown in Table 1, where f_2 is the mole fraction of MI in

Table 1
Composition and T_g data for a series of poly(methylacrylate-*stat*-maleimide) copolymers (EA — elemental analysis)

f_2 (mole fraction)	F_2 (mole fraction) NMR	F_2 (mole fraction) EA	T_g (°C)
0.06	0.04	0.06	25
0.13	0.11	0.11	40
0.20	0.14	0.15	50
0.30	0.22	0.21	80
0.40	0.29	0.32	102
0.50	0.38	0.39	136
0.60	0.46	0.47	181
0.70	0.55	0.53	236
0.80	0.61	0.63	291

the feed and F_2 the mole fraction of MI in the copolymers. Analysis of these data using the "terminal model", as described elsewhere [21] gave values for the monomer reactivity ratios of $r_1 = 0.32 \pm 0.02$, and $r_2 = 1.24 \pm 0.06$.

Also shown in Table 1 are the glass transition temperatures. A sample of poly(maleimide) was prepared and although this polymer starts to degrade at 360°C before any T_g can be detected, a value of T_g about 580°C can be deduced from the trend in the T_g data shown in Table 1, which is well above the degradation temperature.

3.2. Poly(styrene-stat-7[2-methacryloyloxy]ethyl adenine), S/MAAd

Copolymers were prepared from various feed mixtures of S (1) and MAAd (2), with conversions limited to $< 5\%$ to minimise composition drift. While the copolymer compositions were measured by ^{1}H NMR by taking the ratio of the integrals of the peak for one of the purine protons at $\delta = 8.3$ and the aromatic protons in styrene, this was found to be unreliable because of the overlap with the second purine proton. Elemental analysis was used to determine the compositions listed in Table 2. Analysis of these data gave monomer reactivity ratios of $r_1 = 0.69 \pm 0.04$ and $r_2 = 0.41 \pm 0.01$. Also shown in Table 2 are the values of T_g and it can be seen that the T_g–composition relationship is close to an ideal linear dependence with a slight positive deviation.

Table 2
Characterisation data for poly(styrene-*stat*-7-[2-methacryloyloxy] ethyl adenine) copolymers

f_2 (mole fraction)	F_2 (mole fraction)	T_g (°C)
0	0	101
0.05	0.08	111
0.10	0.17	122
0.15	0.25	131
0.20	0.27	130
0.22	0.33	137
0.24	0.38	143
0.33	0.47	144
0.50	0.53	145
0.60	0.60	147
0.75	0.73	171
1.00	1.00	180

Table 3
Composition and T_g data for poly(methyl methacrylate-*stat*-7-[2-methacryloyloxy] ethyl adenine) copolymers (EA — elemental analysis)

f_2 (mole fraction)	F_2 (mole fraction) EA	T_g (°C)
0	0	120
0.05	0.05	123
0.10	0.10	127
0.15	0.21	134
0.20	0.27	140
0.30	0.37	150
0.40	0.50	148
0.50	0.55	159
0.70	0.79	170
0.80	0.83	173
1.00	1.00	180

3.3. Poly(methylmethacrylate-stat-7-[2-methacryloyloxy] ethyl adenine), MMA/MAAd

The compositions of a series of copolymers, prepared from monomers MMA (1) and MAAd (2), were determined using ^{1}H NMR and elemental analysis. Again the NMR data were regarded as being less accurate because the spectral lines were rather broad and the elemental analyses were used. The data are recorded in Table 3 and were used to calculate the monomer reactivity ratios as $r_1 = 0.747 \pm 0.03$, and $r_2 = 1.41 \pm 0.05$. The T_g values, also recorded in Table 3, had a linear dependence on copolymer concentration and tend to follow ideal behaviour.

3.4. Poly(methylacrylate-stat-vinyl cytosine), MA/Vcy

Three samples of MA/Vcy copolymer were prepared and the compositions were determined by elemental analysis. The composition and T_g results are listed in Table 4 where Vcy is monomer 2.

3.5. Binary polymer blends

Three sets of blends were examined; two in which there is a complementary match of the hydrogen bonding sites, i.e. (MA/MI + S/MAAd) and (MA/MI + MMA/MAAd), and a third (S/MAAd + MA/Vcy) in which the adenine and

Table 4
Composition and T_g data for poly(methyl acrylate-*stat*-vinyl cytosine) copolymers

f_2 (mole fraction)	F_2 (mole fraction)	T_g (°C)
0	0	9
0.15	0.19	97
0.25	0.21	116
0.40	0.31	140

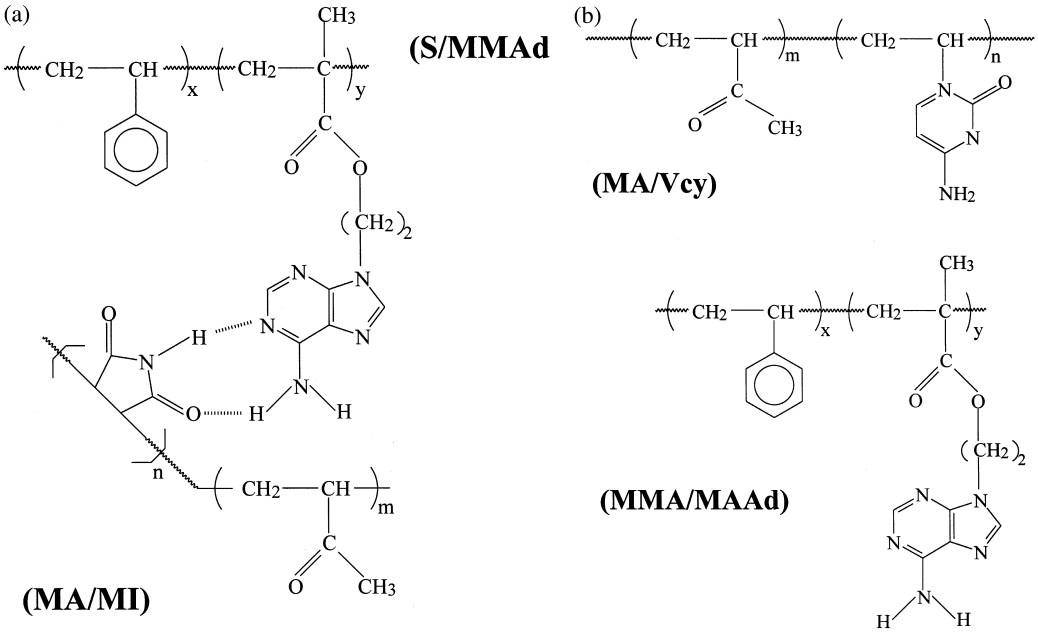

Fig. 1. Structures used for selective blending.

cytosine units do not normally form stable hydrogen bonded structures. In the former the MI (AD) unit can form a double hydrogen bond with the adenine (DA) unit, whereas the cytosine unit with a DDA combination can form triple hydrogen bonded structures in nature with guanine an (AAD) unit but should not form a stable hydrogen bonded combination with adenine. The structures involved are shown in Fig. 1.

The presence of either one T_g or two T_gs in the blends was taken as a measure of miscibility and immiscibility, respectively.

3.5.1. The (MA/MI + S/MAAd) blend system

The miscibility of a range of blends in which a 50:50 mix of the copolymers, with different concentrations of hydrogen bonding units, was determined and the relevant T_g data are listed in Table 5. It can be seen that when the MI and MAAd units are present in roughly equal molar concentrations, the blends are immiscible up to about 15–17 mol% of the hydrogen bonding unit.

For any blend in which one or both components had hydrogen bonding units in excess of 15 mol%, miscible, one phase, blends were obtained as indicated by a single T_g.

Obviously, for steric reasons not every available site in the blend will be capable of forming a successful pairing and only a proportion of the bonding units will contribute to the promotion of miscibility. Thus if, as in blend number 5 the (MA)MI component has only 15 mol% MI, a miscible blend

Table 5
T_gs of poly(MAAd-*co*-S) and poly(MA-*co*-MI) blends

Blend	MAAd (mol%)	MI (mol%)	T_g (°C) MAAd/S	T_g (°C) MA/MI	T_g (°C) blend
1	8	6	111	25	112,23
2	11	11	114	40	118,40
3	17	11	122	40	112,34
4	17	15	125	50	120,56
5	25	15	131	50	64
6	27	21	130	80	80 (v. broad)
7	29	12	132	45	126,43
8	29	21	132	80	117
9	33	32	137	102	132
10	33	47	137	181	146
11	38	53	143	236	161
12	47	47	144	181	163
13	47	63	144	291	167
14	53	53	143	236	164
15	60	63	141	291	166
16	100	100	180	> 360	*

is obtained when (S/MAAd) component has an excess of the adenine group, in this case 25 mol%. In this blend there is now an increased probability of MI–Ad interactions taking place because of the greater concentration of Ad units.

This raises the question, what is the minimum number of hydrogen bonding sites required to promote miscibility in this blend? Inspection of blend 7 (Table 5) with a mixture of 27 mol% Ad and 12 mol% MI, shows it to be just on the edge of miscibility, so one would estimate that the minimum number of sites needed to promote miscibility would have to exceed 12 mol% on each component. This point will be discussed later. All the other blends with concentrations of hydrogen bonding sites greater than 20 mol% exhibit one T_g and are miscible.

It can also be seen that the T_gs of the blends increase with increasing concentration of secondary bonding units in the copolymers up to about 50 mol% after which the T_gs tend to plateau around 166°C. This suggests that the hydrogen bonding is now so great that it has little further significant effect on the chain mobility in the blends.

3.5.2. (MA/MI + MMA/MAAd) blends

In this blend series the same complementary (MI/MAAd) interactions were studied but replacement of styrene by MMA as comonomer means that initially the blends are less immiscible as judged by the smaller $\Delta\delta$, calculated for this blend pairing. The thermal analysis results are listed in Table 6 and it can be seen that miscible one phase blends are obtained using much lower concentrations of the D and A units. Thus in blend 19, a single T_g is observed for components containing only 10 mol% MAAd and 11 mol% MI. All blends with higher levels of D/A sites formed miscible blends, while those with less than 10 mol% were immiscible. Once again the T_gs increased with increasing (D/A) site concentration up to 56–63 mol% then tended to level off.

3.5.3. Miscibility control

The formation of a miscible, one phase, binary polymer blend becomes possible when the free energy change on mixing (ΔG^m) is negative. As the entropy of mixing makes very little contribution to ΔG^m in polymer mixtures, the value of the latter is controlled largely by the ΔH^m term. Using a simplistic argument one can say that if the solubility parameters δp of the blend components are similar, i.e. $\Delta\delta p$ is small, then ΔH^m will also be small, but positive. In this case only a small additional favourable interaction energy would be required to make ΔG^m negative. As $\Delta\delta p$ becomes larger, then a greater increase in the favourable interaction energies is necessary to bridge the gap, i.e. the number of favourable hydrogen bonds formed would have to rise. Thus in the case of the (MA/MI + S/MAAd) blends one needs 12–15 mol% D/A units to promote miscibility, whereas only 10 mol% D/A units was sufficient for the (MA/MI + MMA/MAAd) blends. Estimates of $\Delta\delta p$ show that this is smaller for the latter blends than the former which is consistent with the arguments presented. However, the chain stiffness and packing abilities of the blends could also affect the accessibility of D/A groups for bonding and could be another factor influencing the promotion of miscibility in these systems.

3.5.4. Non-complementary D–A interactions: (S/MAAd + MA/Vcy) blends

In order to test the principle that polymer components containing non-complementary hydrogen bonding structures will fail to form miscible blends the copolymers (S/MAAd) containing adenine were mixed with (MA/Vcy) copolymers containing up to 31 mol% of cytosine. In all cases two T_gs were observed and the blends were deemed immiscible. This is consistent with the behaviour of adenine and cytosine in DNA, where they will not normally bond with each other. While very low levels of mismatched base pairing has been detected in DNA strands [19] this requires the adenine to be either in a protonated form or in its tautomeric structure. These are unlikely to be formed under the conditions used here for blend preparation.

Thus molecular recognition seems to be a feasible tool to use in selective blending and specific structural organisation. Asanuma et al. [22] have demonstrated that poly(2-vinyl-4,6-diamine-1,3,5-triazine) binds uracil and thymine selectively from a solution also containing adenine and cytosine. The triazine rings have a DAD configuration and form triple hydrogen bonds with the complementary ADA groups in uracil and thymine but not with the DAA configuration of cytosine or adenine. This principle has also been demonstrated here for polymer mixtures, but the use of molecular recognition could be used more constructively. For example, polymer blocks with appropriate binding sites

Table 6
Thermal analysis of poly(MAAd-*co*-MMA) blended with poly(MA-*co*-MI)

Blend	MAAd (mol%)	MI (mol%)	T_g (°C) MAAd/MMA	T_g (°C) MA/MI	T_g (°C) blend
17	5	6	123	25	120,27
18	5	12	123	45	119,40
19	10	11	127	40	82
20	21	32	134	102	125
21	27	32	140	102	128
22	37	53	150	236	177
23	55	53	159	236	179
24	50	63	148	291	191

could be linked with complementary sites on other blocks but reject non-complementary units and so build carefully designed structures. This will be explored in a future publication.

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