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Polymer 40 (1998) 227–231

polymer

Modification of poly(styrene-stat-acrylonitrile) to promote polymer blend miscibility through hydrogen-bonded (2,4-diamino-1,3,5-triazine)–maleimide interactions

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Received 28 January 1998; revised 12 March 1998

Abstract

The acrylonitrile units in poly(styrene-stat-acrylonitrile) (SAN) have been partially converted to the 2,4-diamino-1,3,5-triazine (DAT) moiety by the reaction with dicyandiamide in dry dimethyl sulfoxide, containing catalytic amounts of potassium hydroxide. This produced a range of terpolymers of poly(styrene-stat-acrylonitrile-stat-vinyl 2,4-diamino-1,3,5-triazine) with mol% composition in the range (54.3:43.0:2.7) to (54.3:25.0:20.7). Copolymers of methyl acrylate (MA) and maleimide (MI) were also synthesised and used to prepare blends with the modified SAN terpolymers. Here the triazine rings and the maleimide units can form complementary pairs of donor–acceptor–donor (DAD) and (ADA), triple hydrogen bonding sites. It was found that miscible, one-phase, polymer blends could be formed if the DAT content of the modified SAN terpolymers was ≥ 10 mol% and the MI content of the (MA–MI) copolymers was > 22 mol%, or alternatively if the MI content was 9–14 mol% and the corresponding DAT content in the modified SAN was ≥ 21 mol%. Once formed these secondary interactions were stable up to the onset of degradation of the blends and there was no evidence of a lower critical temperature for phase separation. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Site-specific interactions; (Styrene–acrylonitrile–vinyl triazine) terpolymers

1. Introduction

The use of secondary bonding interactions to promote miscibility in polymer blends has been the subject of a wide range of studies [1,2]. Such secondary interactions include hydrogen bonding [3–5], ion–dipole interactions [6–8] and charge-transfer (C-T) complexation [9–12]. In many instances suitable donor (D) and acceptor (A) sites will be an integral part of the unmodified polymer structures, but the interactions between a D group on one molecule and an A group on another may be undiscriminating, i.e. the D group can interact with any suitable A group independent of the structure. This would not necessarily be the case for C-T complex formation where interaction would only occur if the appropriate D–A pairings were available. This is the principle used in nature where in DNA the pyrimidine–purine base pairings are quite specific with guanine–cytosine and adenine–thymine (uracil) being the preferred combinations, interacting through triple and double hydrogen bonding, respectively.

An active area of research now involves the modification of existing polymers to introduce the appropriate D and A sites where a D group recognizes only a structurally complementary A group and rejects, or has a lower probability of interacting with, other A groups. This type of site-specific secondary bonding can be used to build controlled structures and is now being used in supramolecular polymer chemistry to encourage the self assembly of macromolecules into particularly designed structures. The D and A groups used normally have the capability of forming double or triple hydrogen bonds, and are often structural analogues of the pyrimidine–purine base pairs. Typical examples of this approach are seen in the work of Stadler and co-workers [13,14] who have grafted (4-carboxy phenyl) urazole groups on to polybutadiene to give a two-dimensional network, formed by self association of the urazole moieties, whereas Rebek [15] has used melamine to form triple hydrogen-bonded structures with trisimide units. Melamine was used to complex with maleimide copolymers by Lange and Meijer [16,17] who also incorporated the analogous vinyl triazine into copolymers as a specific bonding site. Lehn and co-workers [18] employed the complementary pairing of

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PII: S0032-3861(98)00236-5

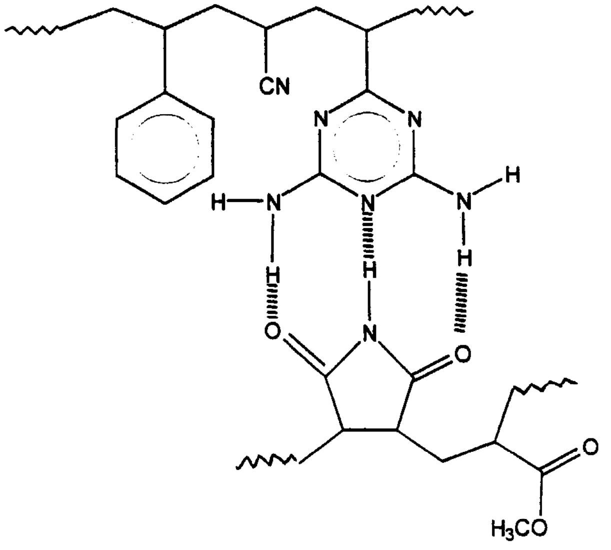


Fig. 1. Schematic diagram showing the triple hydrogen bond interaction between the maleimide unit and the triazine ring in the modified SAN terpolymer.

uracil and 2,6-diacyl aminopyridine groups to link telechelic tartaric acid derivatives or telechelic rigid rod-like dianhydride units [19] through triple hydrogen bond formation. In each case the telechelic molecules had one or other of the units at the chain ends and end-to-end association was obtained, giving linear chain extension as opposed to the more intimate polymer blending obtained in the previous examples.

While we have carried out similar work to Lehn using instead C-T groups on the telechelic molecules [20], the approach adopted here was to modify poly(styrene-stat-acrylonitrile) (SAN) to widen its range of miscibilities and blending capabilities with other polymers. This was achieved by converting the cyano group to the 2,4-diamino-1,3,5-triazine ring and assessing the effect of this triple hydrogen bonding (DAD) unit on the miscibility with copolymers of methylacrylate and maleimide where the latter provides a complementary (ADA) bonding site for the triazine ring. The structures are shown in Fig. 1.

2. Experimental section

2.1. Reagents

Poly(styrene-stat-acrylonitrile), 30 wt.% acrylonitrile (SAN); dimethyl sulfoxide (DMSO), anhydrous 99.8%; methylacrylate (99%); maleimide (99%); and dicyandiamide (DCDD) were obtained from Aldrich. Potassium hydroxide was purchased from Fischer Scientific.

2.2. Modification of SAN

A typical procedure was as follows: a solution of SAN (1.766 g) in DMSO (110 cm^3) was prepared under a dry nitrogen atmosphere. DCDD (1.682 g) and KOH (0.281 g) were then added and the reaction mixture was heated to 340–350 K for varying lengths of time, depending on how far the conversion of the nitrile group to the triazine ring was allowed to proceed (see Table 1). The modified SAN samples were recovered by reducing the solvent volume and precipitating the terpolymer using methanol. Purification was achieved by re-dissolving the terpolymer in dichloromethane or DMSO and re-precipitating the samples by addition to methanol. This was repeated and the product was dried finally under vacuum.

2.3. Copolymer synthesis

Copolymerizations of methylacrylate and maleimide using various monomer feed ratios, were carried out in dry tetrahydrofuran using 0.25 mol% of α,α^1-azo bisiso butyronitrile as initiator. Reactions were carried out under vacuum at 313 K and terminated after about 10% conversion to minimize composition drift. Products were isolated by precipitation in methanol, and all samples were then dried for at least 48 h in a vacuum oven at 310 K.

2.4. Characterization of copolymers

The compositions of the copolymers were determined both by elemental analysis and ^1H n.m.r. using deuterated

Table 1
Conversion of acrylonitrile (AN) in SAN to triazine rings and the glass transition temperatures of the terpolymers

Reaction time (h)	Conversion (%)	Triazine units (mol.%)	Residual AN[a] (units/mol.%)	T_g (K)
0.00	0	0	45.7	378
1.00	5.8	2.7	43.0	398
2.00	12.2	5.6	40.1	407
3.25	20.2	10.2	35.5	418
4.00	25.0	11.4	34.3	423
6.00	29.8	13.6	32.1	429
9.00	35.6	16.3	29.4	434
13.00	39.5	18.1	27.6	440
21.00	45.5	20.7	25.0	451

[a] The styrene content remained at 54.3 mol.% throughout

DMSO as solvent. Spectra for the latter were measured using a Bruker WP-200 SY instrument and compositions were calculated by comparing the integrals of the imide proton on the maleimide ($\delta = 11.3$) with those of the methoxy protons on the methyl acrylate units ($\delta = 3.6$).

The compositions calculated using both methods agreed to within ± 2 mol%.

2.5. *Characterization of terpolymers*

Terpolymer compositions were determined using elemental analysis. Each sample was also analysed using a Perkin-Elmer 1720X FTIR, and all modified materials exhibited the following characteristic wave numbers (cm^{-1}): N–H stretch (triazine ring) 3469, 3324, 3195; C–H aromatic stretch (styrene) 3084, 3061, 3028; C–H stretch main-chain 3004, 2927, 2859; C≡N stretch (acrylonitrile) 2238, C=C stretch aromatic 1603, 1494, 1454; N–H deformation (triazine ring) 1548; and C–H deformation aromatic 762, 702.

2.6. *Glass transition temperatures (T_g)*

The glass transition temperatures were measured using a Perkin-Elmer DSC IV, at a heating rate of 20 K min^{-1}. The T_g was taken as the onset point of the baseline shift experienced during the transition. The T_g values were also measured at 1 Hz, using a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA).

3. Results and discussion

Conversion of the cyano group to the 2,4-diamino-1,3,5-triazine ring progressed smoothly, according to Scheme 1, under the conditions used, viz. very dry DMSO and catalytic amounts of KOH [21]. Approximately half of the acrylonitrile units in the selected SAN sample were converted in 24 h, and the reaction tended to slow down as the triazine ring content increased. The additional steric hindrance introduced by the triazine ring led to a progressive increase in the T_g of the terpolymer, as indicated by the data shown in Table 1, and may also restrict the conversion of the remaining cyano units.

The triazine ring now provides a potential triple hydrogen bonding (donor–acceptor–donor (DAD)) site which can be satisfied by a complementary ADA site. Such a unit can be provided by maleimide and the influence of these units on polymer miscibility was tested using poly(methylacrylate-stat-maleimide) copolymers (MA–MI) blended with the modified SAN terpolymers (mod SAN).

3.1. *Blending studies: SAN/(MA–MI)*

Miscibility of the copolymer–copolymer and copolymer–terpolymer blends was established using the criteria of optical clarity, and T_g measurements obtained from both d.s.c. and DMTA studies, where a single T_g for the blend was used as an indication of a one-phase system. The SAN/(MA–MI) (50/50, w/w) blends were examined first. Samples were prepared by dissolving both components in DMSO and mixing the solutions, followed by co-precipitation into water. In all cases the blends obtained exhibited two glass transitions and when films were cast from the blend solutions in chloroform, these were opaque. This established that the unmodified SAN was immiscible with the (MA–MI) copolymers in the composition ranges of the latter to be examined with the mod-SAN samples.

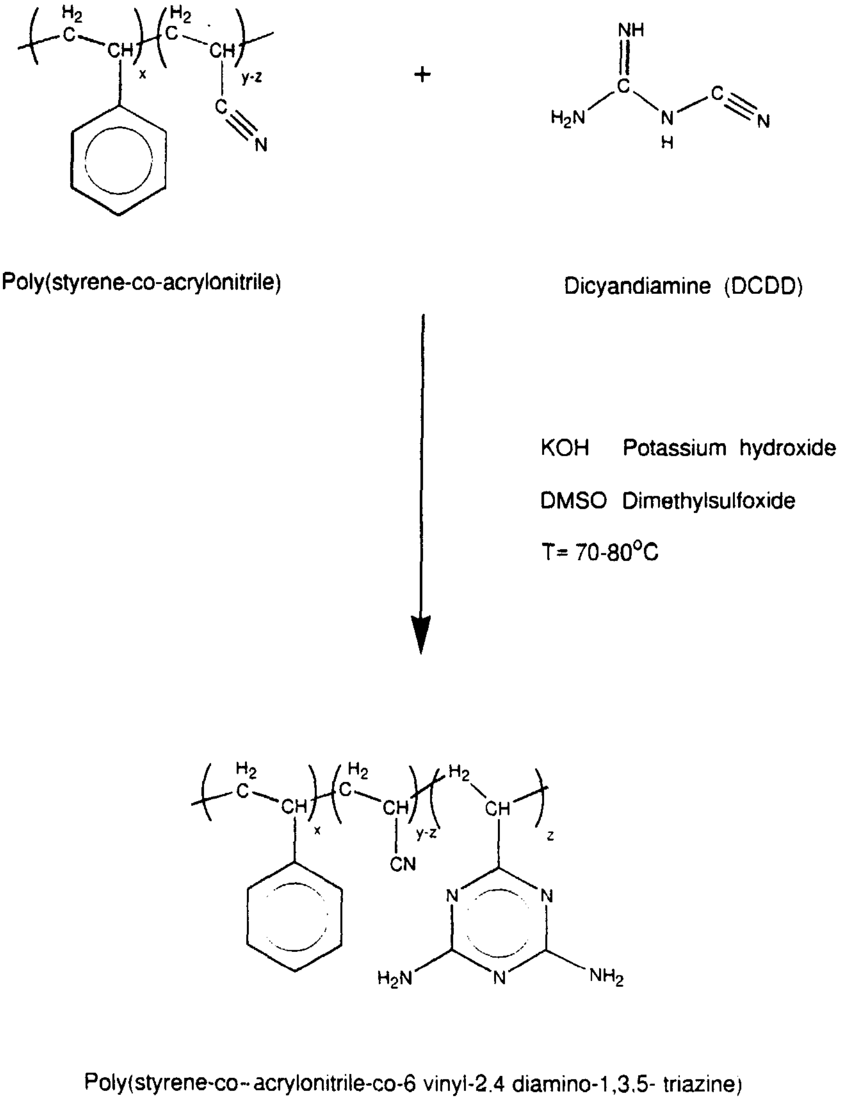
3.2. *Mod-SAN/(MA–MI)*

Blends were prepared by coprecipitation from DMSO solutions into water or films were cast from DMSO solutions. The results are summarized for three sets of blends in Table 2 and Table 3. When the SAN had been modified to contain 10 or 11.4 mol.% of the triazine ring the results indicate that the mol.% of MI in the second component had to be MI > 22 mol.% if a one-phase blend was to be obtained. While the d.s.c. measurements could be ambiguous for (MA–MI) copolymers with MI ≤ 22 mol.% because the transitions observed were usually very broad, the DMTA measurements were much more sensitive and exhibited two distinct damping peaks indicating a two-phase system in blends 1–4 and 8. Single T_g values which were sharply defined using both techniques were observed for blends 5–7 and 10. If the mol.% of the triazine was increased to 21 mol.% then one-phase blends could be obtained for MI ≥ (9–14) mol.%. These results suggest that the triazine rings and the MI units are equally accessible for bonding but that for one-phase miscible blends to be formed a minimum mol.% content of either had to be at least 10 mol.% and that the amount of the complementary bonding site had to be at least twice that amount. This probably reflects the more rigorous steric requirements of a triple hydrogen bond formation. While 10 mol.% is a minimum site content on one component, an excess of the complementary bonding site is required to raise the probability that the number of effective bonding sites needed to promote miscibility is increased, i.e. there is a greater chance of the majority of the 10 mol.% sites being involved in hydrogen bonding, when there is an excess of the complementary site. Thus, the presence of 10 mol.% of the triazine ring in the mod-SAN does not lead to a sufficient level of associated hydrogen-bonded sites if only 10 mol% of maleimide is available on the complementary copolymer in the blend.

It is difficult to be more precise about the ratio of the bonding to non-bonding sites in these systems. The FT-i.r. spectra exhibited peak shifts which indicated the presence of hydrogen bonding in the blends, but these could not be quantified with sufficient accuracy to allow this to be estimated.

In any polymer blend system, where miscibility is

Scheme of reaction



Scheme 1.

Table 2
Miscibility of mod-SAN (10.2, 11.4)/(MA–MI) blends established by optical clarity, d.s.c. and DMTA measurements

Blend number	mod-SAN		(MA–MI)		Blends			
	mol.% triazine	T_g (K)	mol.% MI	T_g (K)	Optical clarity	D.s.c. T_g (K)	DMTA T_g/K	Miscibility
1	10.2	418	2	286	Opaque	Broad	Two	No
2	10.2	418	3	293	Opaque	Broad	Two	No
3	10.2	418	14	330	Opaque	Broad	Two	No
4	10.2	418	22	355	Clear	Two	Two	No
5	10.2	418	27	368	Clear	410	423	Yes
6	10.2	418	39	409	Clear	412	425	Yes
7	10.2	418	44	441	Clear	425	428	Yes
8	11.4	423	7	305	Opaque	Broad	Two	No
9	11.4	423	22	355	Clear	Broad	Broad	Limit
10	11.4	423	27	368	Clear	415	427	Yes

Table 3
Miscibility of mod-SAN (21.0)/(MA–MI) blends established by optical clarity, d.s.c. and DMTA measurements

Blend number	mod-SAN		(MA–MI)		Blends			
	mol.% triazine	T_g (K)	mol.% MA	T_g (K)	Optical clarity	D.s.c. T_g (K)	DMTA T_g (K)	Miscibility
11	21	451	2	286	Opaque	Two	Two	No
12	21	451	3	293	Opaque	Two	Two	No
13	21	451	9	305	Clear	Two	Two	No
14	21	451	14	330	Clear	375	—	Yes
15	21	451	22	355	Clear	400	—	Yes
16	21	451	27	368	Clear	405	—	Yes
17	21	451	39	409	Clear	442	454	Yes
18	21	451	44	441	Clear	445	457	Yes

promoted by D–A interactions only a proportion of the total number of sites will be physically capable of interacting with the appropriate complementary sites. Single hydrogen bonding site interactions should be more facile as the steric requirements for multiple hydrogen bonding interactions are probably more rigorous. However, having once formed, the multiple bonding sites will have a greater bonding strength and in the miscible blends studied here there was no evidence of phase separation on heating. Samples showed no evidence of a lower critical temperature phase boundary and tended to degrade without phase separation on heating to high temperatures, indicating that the hydrogen bonding was very stable.

While the required minimum concentration of bonding sites required to promote miscibility has been established as > 10 mol.% in this system, the amount will depend on how incompatible the two components of the blend are to begin with. A rough guide to this would be to examine the difference in the cohesive energy densities of the two components, where large differences would require correspondingly higher levels of secondary bonding to overcome the repulsive forces acting between the two components than those where the differences were small. Hence, multiple bonding sites may have no significant advantage over single bonding interactions in promoting miscibility in polymer blends unless selective binding is required to produce specific structures.

4. Conclusions

At least 50 mol.% of the acrylonitrile units in poly (styrene-stat-acrylonitrile) can be readily converted to the triple hydrogen bonding unit 2,4-diamino-1,3,5-triazine. The latter can form hydrogen bonds with the complementary unit maleimide (which can be regarded as an analogue of uracil) and this interaction can be used to promote miscibility in blends of the modified SAN with copolymers of methyl acrylate and maleimide. This opens up the possibility that these moieties could be used as selective, specific interacting sites which would tend to interact as a pair and reject other sterically unsuitable secondary bonding sites. This will be the subject of future publications.

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