

# Hydrogen Bonding Interactions of Styrene-Maleimide Copolymers with Diaminotriazine Derivatives

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**ABSTRACT:** Poly(styrene-*co*-*N*-maleimide) precursor and poly(styrene-*co*-*N*-maleimide)-*block*-polystyrene have been synthesized by quasilinging radical polymerization. Low molecular weight compounds with the sites specific for the complementary binding to the maleimide moieties via triple hydrogen bonds, 2,4-diamino-6-*n*-alkoxy(C-4, C-8, and C-12)-s-triazines, have been prepared. Hydrogen bonding

between diaminotriazine and maleimide units in the copolymer-diaminotriazine mixtures has been investigated by FTIR. Microphase separated structure in the block copolymer-diaminotriazine mixtures has been confirmed by DSC. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2338–2346, 2006

**Key words:** host-guest systems; DSC; FTIR

## INTRODUCTION

Polymers with desired parameters synthesized in a controlled or living way and having sites suitable for hydrogen bonding with complementary functional low molecular weight compounds via molecular recognition are very attractive for the applications in advanced technologies. Variation of the chemical structure and architecture of the polymer and hydrogen-bonded compound and stoichiometry of their mixtures offer a convenient way to control the morphology and to tune properties of the materials prepared.<sup>1</sup>

In recent years, there has been an increasing interest in preparation and investigation of polymer supramolecular hydrogen bonding complexes. Hydrogen bonding of alkylphenols to vinylpyridine-based polymers and copolymers was investigated by Ruokolainen et al.<sup>2–4</sup> However, these and other systems based on formation of single hydrogen bonds are not able to exploit fully the phenomenon of the molecular recognition.

To overcome this drawback, multiple hydrogen bonding in polymer complex preparation has been used and investigated by several research groups. For example, Rotello and coworkers<sup>5–7</sup> investigated the complex formation between polystyrenes (partially) functionalized with diaminotriazine (DAT) and diacyl diaminopyridines moieties and flavin via triple hydrogen bonding formation. Stubbs and Weck<sup>8</sup> synthesized a series of DAT and diaminopyridine functionalized norbornene monomers, which were polymerized into fully functionalized polymers. Complex formation and self-assembly process of these monomers and polymers with *N*-butylthymine were investigated. Asanuma et al.<sup>9,10</sup> used poly(2-vinyl-4,6-diamino-1,3,5-triazine) for selective binding of the derivatives of thymine and uracil through the formation of triple hydrogen bonds with DAT units.

All the studies mentioned above are based on the molecular recognition motif shown in Scheme 1, with donor-acceptor-donor structure being a part of the polymer. Systems with the reverse structure, i.e., ADA on the polymer containing, e.g., maleimide (MI) moieties hydrogen-bonded to derivatives of DAT or diaminopyridine are also admissible. Actually, the ability of MI to form multiple hydrogen bonds has been already used in compatibilization of styrene-MI copolymers with poly(methyl methacrylate) and poly(2-vinylpyridine) by Vermeesch and Groeninckx<sup>11</sup> and Vermeesch et al.<sup>12</sup> Lange and Meijer<sup>13</sup> investigated supramolecular polymer interactions of the styrene-MI copolymer with melamine and poly(styrene-*co*-2,4-

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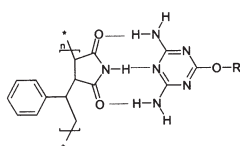
diamino-6-vinyl-*s*-triazine). Cowie and Cocton<sup>14</sup> investigated the role of triple hydrogen bond formation in blending of the copolymers containing complementary MI and DAT moieties. In another study, Cowie and Love<sup>15</sup> used methylacrylate-MI copolymers to prepare miscible blends with copolymers of styrene with a monomer complementary to MI units such as, e.g., vinylcytosine or ethyladenine via triple hydrogen bonding.

The survey of the Cambridge Structural Database for the occurrence of various hydrogen-bonded structures in crystals, made by Allen et al.<sup>16</sup> ranks the motif utilized in this work (see Scheme 2) among one of the most frequent and due to its similarity with nucleotide recognition in DNA as a very promising in supramolecular chemistry.<sup>17</sup>

In addition to the desirable interassociation of MI to DAT via triple hydrogen bonds, intra- and interchain self-association of the MI units resulting in dimer and multimer formation and self-association of DAT must be also taken into account as shown in Scheme 1.

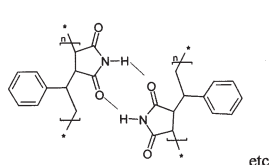
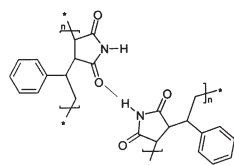
Value of the equilibrium self-association constant found for MI or succinimide in nonpolar solvents like CCl<sub>4</sub> was found to be within 10–60 mol<sup>-1</sup> L, as reported in Ref. 18. In more polar solvents, like CHCl<sub>3</sub>,

Inter-association MI-DAT:



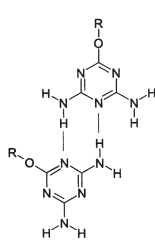
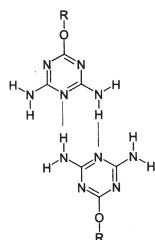
Self-association:

a) MI-MI

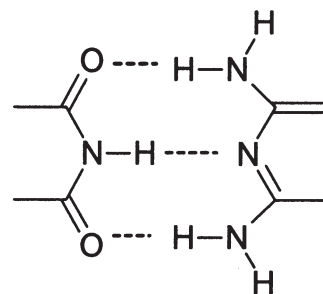


etc

b) DAT-DAT



**Scheme 1** Types of hydrogen bonding in MI-DAT systems.



**Scheme 2** Triple hydrogen bonding between MI and triaminotriazine units.

the values become lower than 10 mol<sup>-1</sup> L, cf, as reported in Ref. 19. The value of the self-association constant for 2,4-diamino-6-*n*-dodecyl-*s*-triazine in CHCl<sub>3</sub> found by Beijer et al.<sup>20</sup> is about 2 mol<sup>-1</sup> L. The same authors also investigated interassociation of a few triazine derivatives with complementary molecules, such as, e.g., uracil derivatives. Values of the interassociation constant found are two orders higher in magnitude than the value of the self-association constant (890 mol<sup>-1</sup> L and 750 mol<sup>-1</sup> L, with 1*N*-propylthymine and 1*N*-methyl-6-tridecyluracil, respectively).

In the solid state at room temperature, diamino-triazine derivatives are crystalline. Crystalline structure of a series of DAT derivatives was resolved by Díaz-Ortiz et al.<sup>21</sup> who found that, e.g., 2,4-diamino-6-phenyl-*s*-triazine forms monoclinic lattice at 170 K. In this compound, the number of the hydrogen bond donors exceeds the number of acceptors and consequently, not all H atoms of amino groups are involved in the hydrogen bonding. A similar situation can be expected in the case of DATs used in this study.

Self-association of the MI monomer units in styrene-MI copolymers has been studied by Vermeesch et al.<sup>12</sup> Calculation of the values of self-association constant defined in terms of molar concentrations,  $K_a$ , from the values of the (dimensionless) constant defined by means of molar fractions,  $\tilde{K}_a$ , reported in Ref. 12, ( $K_a = \tilde{K}_a c_{MI}$ , where  $c_{MI}$  is the molar concentration of MI units in the bulk polymer system) leads to the value  $K_a = 0.4$  mol<sup>-1</sup> L at 30°C. Unfortunately, we were unable to find any reported values of the interassociation constants of MI monomer units with other compounds in solid state. However, due to the high ability of MI monomer to form complexes with complementary molecules in the solutions, this feature might not be lost after polymerization.

In our study, differential scanning calorimetry (DSC) and Fourier-transformed infrared spectroscopy (FTIR) were used to investigate microphase separation and hydrogen-bonding between polymers containing MI units, namely poly(styrene-*co*-*N*-MI) and poly(styrene-*co*-*N*-MI)-*block*-polystyrene, and alkoxy derivatives of diamino-*s*-triazine.

TABLE I  
Characteristics of the Copolymers

Symbol	Copolymer	$f_{MI}^a$	$w_{PS}^b$	$M_n^c$	$M_w/M_n^d$	$T_g^e$ (°C)	$\Delta c_p^f$ (J K <sup>-1</sup> g <sup>-1</sup> )
C	poly(styrene- <i>co</i> -maleimide)	0.37	–	15,200	1.27	211	0.33
BC	poly(styrene- <i>co</i> -maleimide)- <i>block</i> -polystyrene	–	0.82	29,400	1.72	102 <sup>g</sup> , 220 <sup>h</sup>	0.245 <sup>g</sup> , 0.03 <sup>h</sup>

<sup>a</sup> Molar fraction of MI in the polymer determined by from elemental analysis.

<sup>b</sup> Weight fraction of PS determined from elemental analysis.

<sup>c</sup> Polystyrene-equivalent molecular weight determined by SEC.

<sup>d</sup> Polydispersity index.

<sup>e</sup> Glass transition temperature determined by DSC from the second scan.

<sup>f</sup> Change in the heat capacity determined by DSC from the second scan.

<sup>g</sup> PS block.

<sup>h</sup> P(S-*co*-MI) block.

## EXPERIMENTAL

### Materials

#### Maleimide copolymers

Poly(styrene-*co*-*N*-MI) (C) and poly(styrene-*co*-*N*-MI)-*block*-polystyrene (BC) were synthesized by nitroxide-mediated radical polymerization.<sup>22</sup> C: A solution of styrene (S), maleimide (MI) ( $5 \times 10^{-2}$  mol of comonomers), and stable nitroxyl radical TEMPO ( $1.5 \times 10^{-4}$  mol) in diglyme (10 mL) was heated at 125°C in a sealed glass ampoule in nitrogen atmosphere. Mole fraction of MI,  $F_{MI}$ , was 0.2. After 2 h, the resulting TEMPO-terminated copolymer was precipitated from the reaction mixture with excess ethanol. It was dried under vacuum (6.6 Pa) at room temperature. BC: The obtained copolymer C (0.2 g), styrene (5 mL), and diglyme (10 mL) in a glass ampoule were heated at 125°C in nitrogen atmosphere for 40 min. The reaction mixture was poured into a 10-fold amount of ethanol and the isolated diblock copolymer BC was dried under vacuum (6.6 Pa) at room temperature. Characteristics of the polymer precursor C and diblock copolymer BC are given in Table I.

#### Diaminotriazines

2,4-Diamino-6-*n*-alkoxy (C-4, C-8, and C-12)-*s*-triazines (denoted as DAT4, DAT8, and DAT12, see Table

II) were prepared by Williamson synthesis of ethers.<sup>23</sup> General procedure: Sodium (0.1 mol) was dissolved in 100 mL of alcohol dried over molecular sieves in a 250 mL three-necked flask equipped with a condenser and a stirrer. With the higher molecular weight alcohols, gentle heating (100°C for 1-octanol and 150°C for 1-dodecanol) was necessary to effect solution of metal. When the sodium was dissolved, the halotriazine (0.1 mol) was added with continued stirring. Refluxing was continued until the appearance of the suspended solid changed from that of the amorphous halotriazine to that of the crystalline sodium chloride. Then the mixture was filtered hot and the filtrate cooled down to 5°C. The precipitated ether was filtered off and crude product was recrystallized from mixture THF/H<sub>2</sub>O = 1/1. Low-melting impurities from DAT8, which were present after recrystallization, were removed by washing with acetone. The crude DAT12 was purified by dissolving in THF and precipitation with an excess of hexane. Structures of the obtained products were confirmed by melting points and elemental analyses.

#### Preparation of the MI copolymer-DAT mixtures

Before the preparation, both copolymers C and BC were dried in vacuum at 120°C for 2 days. The corresponding polymer (ca 20 mg) was then dissolved in 1

TABLE II  
Characteristics of the DAT Derivatives

Symbol	Compound name	$T_m^a$ (°C)	$\Delta H_m^b$ (J g <sup>-1</sup> )	$\Delta H_m^c$ (kJ mol <sup>-1</sup> )	$\Delta S_m^d$ (J K <sup>-1</sup> mol <sup>-1</sup> )
DAT4	2,4-diamino-6- <i>n</i> -butyloxy- <i>s</i> -triazine	178	133	24.3	53.9
DAT8	2,4-diamino-6- <i>n</i> -octyloxy- <i>s</i> -triazine	122	113	26.9	68.0
DAT12	2,4-diamino-6- <i>n</i> -dodecyloxy- <i>s</i> -triazine	122	79	29.0	73.9

<sup>a</sup> Melting temperature determined from the onset by DSC.

<sup>b</sup> Melting enthalpy determined from the peak area by DSC.

<sup>c</sup> Molar melting enthalpy.

<sup>d</sup> Molar melting entropy.

mL of dry dioxane, followed by a slow addition of the necessary amount of the DAT derivative under rigorous mixing by a magnetic stirrer. The solutions obtained were poured into glass dishes and the solvent was allowed to evaporate at room temperature. The mixture prepared was then dried at 120°C in vacuum for 2 days and stored in a desiccator.

Mixtures of C or BC with DAT4, DAT8, and DAT12 at molar ratios of the MI monomer to DAT being 1:1, 1:0.5, 1:0.25, and 1:0.1 were prepared.

## Characterization

### Differential scanning calorimetry

Calorimetric measurements were performed in a Perkin-Elmer Diamond DSC apparatus. Nitrogen gas was let through the DSC cell with a flow rate of 20 mL/min. The temperature of the equipment was calibrated with indium. The melting heat of indium was used for calibrating the heat flow. The samples were subjected first to a heating scan from 50 to 200°C (or ca 20° above the melting temperature of the DAT if a melting peak was observed), followed by a cooling scan from that temperature to 50°C and, finally, second heating scan from 50 to 200°C. All scans were carried out at a rate of 10°C/min. Glass transition temperatures were determined using the half  $\Delta c_p$  method from the second heating calorigrams.

### Fourier-transformed infrared spectroscopy

Infrared spectra were obtained using a SHIMADZU IRPrestige-21 spectrometer using KBr disks (1 mg and 3 mg of sample for the C and BC systems, respectively, per 100 mg KBr). Approximately 200 scans with spectral resolution 2 cm<sup>-1</sup> were coadded to achieve a good signal-to-noise ratio. To minimize water absorption, before the measurement, the disks were dried in vacuum at 80°C for ca 12 h. All measurements were performed at room temperature and dry air environment.

## RESULTS AND DISCUSSION

### Solubility of the styrene-MI copolymers and DATs

The solubility of the copolymers under study and DATs prepared in nonpolar solvents (like, e.g., CCl<sub>4</sub>) is very low. In CHCl<sub>3</sub>, precursor C is insoluble, however, block copolymer BC swells and forms a gel-like phase. As regards the solubility of DATs in CHCl<sub>3</sub>, DAT4 is almost insoluble, DAT8 is soluble to some extent and DAT12 forms a turbid solution. However, addition of DAT8 to BC swollen in CHCl<sub>3</sub> leads to its dissolution and formation of a clear solution. This can be considered as an indication of the interaction between BC and DAT8 in CHCl<sub>3</sub> solution. Both, the

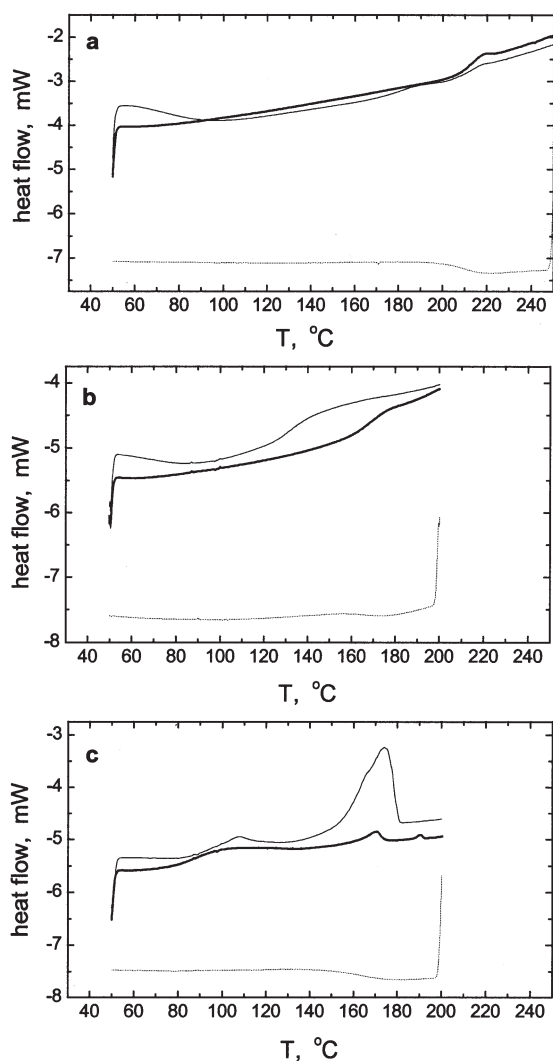
copolymers and DATs are well soluble in polar solvents (e.g., tetrahydrofuran, dioxane, dimethylformamide, or pyridine), which was the reason for using one of them (dioxane) in the preparation of the mixtures.

### DSC evaluation

Values of the melting temperature, melting enthalpy, molar melting enthalpy, and entropy for DAT4, DAT8, and DAT12 determined by DSC are given in Table II. The highest value of melting temperature was found for DAT4, almost equal values were obtained for DAT8 and DAT12. This finding can be explained as the result of interplay between decreasing concentration of the hydrogen bonds in the compound and increasing importance of other secondary interactions per molecule, consequently, a gradual growth of  $T_m$  can be expected for DATs with longer alkyl tail.

Figures 1(a)–1(c) show calorigrams from all DSC steps obtained from the polymer precursor C and its two mixtures with DAT4. Single glass transition is found for C [Fig. 1(a)] at a high temperature ( $T_g = 211^\circ\text{C}$ , see Table I) being the result of both copolymer chain stiffness and intensive hydrogen bonding between self-associated MI monomer units. Similarly, mixtures of C with low content of DAT4 show only single glass transition shifted to lower temperatures as it is illustrated in Figure 1(b) for the mixture with molar ratio [MI]:[DAT4] = 1:0.25. When the DAT4 content in mixtures is further increased, becoming higher than [MI]:[DAT4] = 1:0.50, a peak due to melting of DAT4 appears in the calorigrams. This peak is relatively broad, since DAT4 is present in the form of tiny crystals as it is illustrated in Figure 1(c) for the mixture with [MI]:[DAT4] = 1:1. After the evaporation of the solvent, a part of DAT4 in the mixtures containing higher amount of DAT4 is therefore macrophase separated. In the mixture, C-DAT4 mixture with [MI]:[DAT4] = 1:1, the macrophase-separated fraction of DAT4 represents about 50% of total content, as estimated from the melting peak area. However, subsequent DSC thermal treatment (heating the systems above the melting temperature of the DAT4) leads to the melting of the DAT4 crystals and their dissolution in polymer-rich phase as demonstrated by the significant reduction of the peak observed in the second heating scan. Incorporation of the DAT4 into polymer phase is also reflected in the further shift of the glass transition to lower temperatures. Similar behavior was also found for C-DAT8 and C-DAT12 mixtures. Figure 2 summarizes calorigrams obtained during second heating for all C-DAT mixtures.

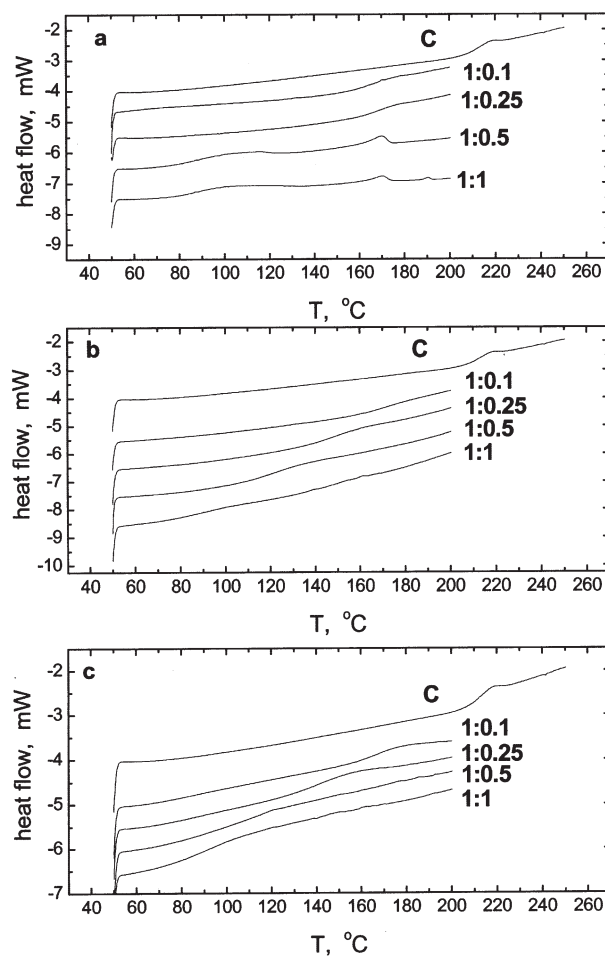
Figure 3 shows the dependences of the inverse glass transition temperature on the weight fraction of DAT,  $w_{\text{DAT}}$ , in the Flory-Fox plot for all the C mixtures. In the range of compositions investigated exper-



**Figure 1** DSC scans of the polymer precursor C and two C+DAT4 mixtures. Molar ratio of MI monomers to DAT: (a) 1:0 (C itself), (b) 1:0.25, and (c) 1:1. Symbols are (—) first heating, (·····) first cooling, and (—) second heating.

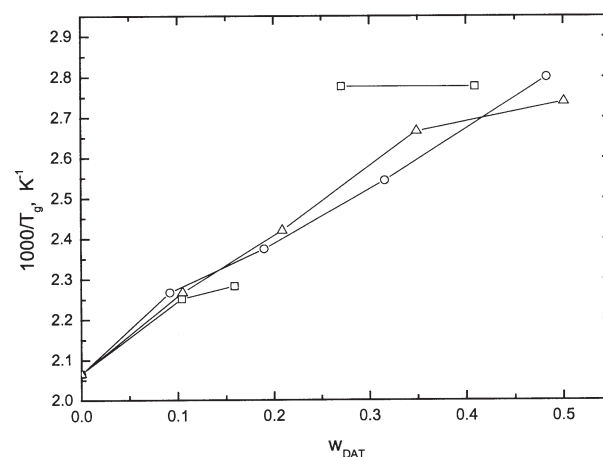
imental data for C-DAT8 and C-DAT12 mixtures follow almost the same increasing curve regardless of the length of alkyl tail in DAT. Since the stiffness of polymer chains is not influenced by mixing, the only factor controlling change of the glass transition in the systems studied is hydrogen-bonding between self-associated MI units. The shift of the glass transition in the mixtures to lower temperatures can be explained by breaking a part of MI-MI hydrogen bonds due to the presence of DAT playing the role of plasticizer. The shift depends only on the volume fraction of DAT and not the length of alkyl tail.

Calorigrams from all heating and cooling steps obtained from the block copolymer BC and its two mixtures with DAT4 are depicted in Figures 4(a)–4(c). Two glass transition temperatures are revealed for the

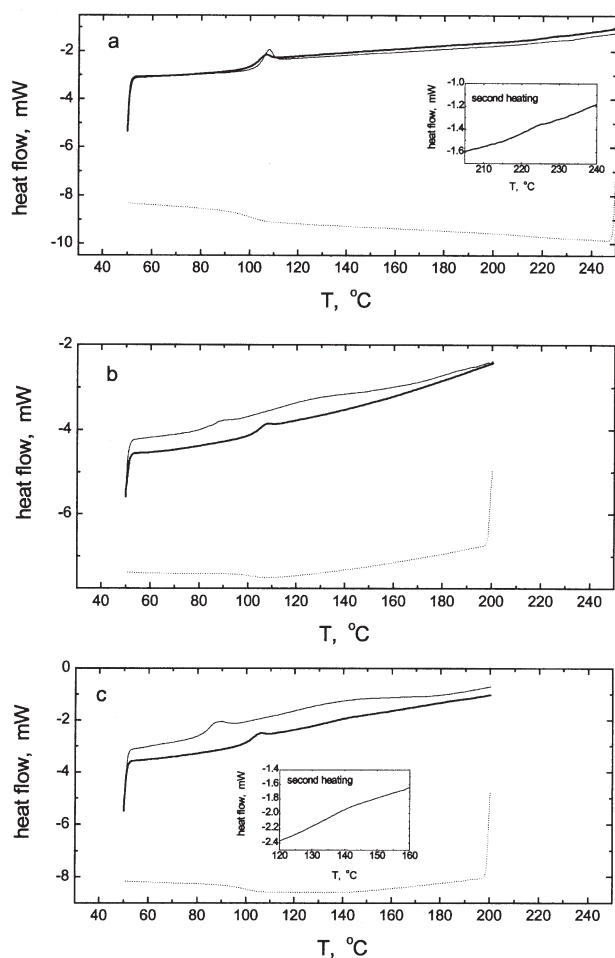


**Figure 2** Second heating DSC scans of the polymer precursor C and its mixtures with (a) DAT4, (b) DAT8, and (c) DAT12.

block copolymer, lower one at ca 102°C (see Table I) for PS block and higher one at ca 220°C for P(S-MI) block as determined from the second heating run [see



**Figure 3** Flory-Fox plot for the mixtures. Symbols are (□) C+DAT4, (○) C+DAT8, and (Δ) C+DAT12.



**Figure 4** DSC scans of the block copolymer BC and two BC+DAT4 mixtures. Molar ratio of MI monomers to DAT: (a) 1:0 (BC), (b) 1:0.25, (c) 1:1. Symbols are (—) first heating, (·····) first cooling, and (—) second heating.

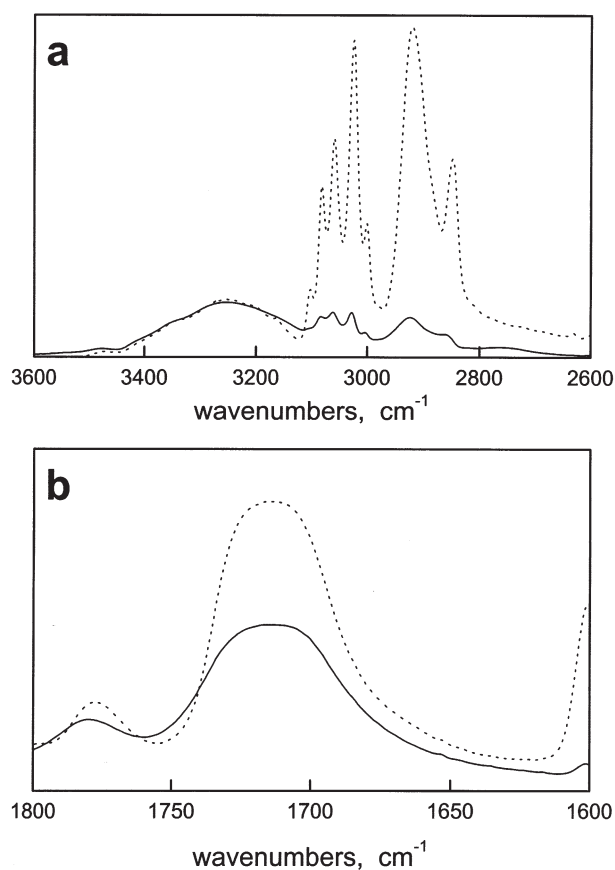
also inset in Fig. 4(a)]. The latter temperature is somewhat higher than the value observed in the polymer precursor C. No melting of DATs has been observed in the mixtures with BC as demonstrated for BC-DAT4 mixtures shown in Figures 4(b) and 4(c). In the first heating scans, glass transition of the PS block in the mixtures occurs at somewhat lower temperatures (ca 15°) than in the second heating scans. In the second heating, the glass transition temperatures of the PS block obtain almost the same value (101°C and 103°C for the [MI]:[DAT4] = 1:0.5 and 1:1 mixture, respectively), which is very close to the value determined for this block in the BC itself (102°C). The other glass transition corresponding to P(S-MI) block was observable only in the second heating of the mixture with [MI]:[DAT4] = 1:1, with  $T_g$  being ca 140°C [see inset in Fig. 4(c)]. We think that these facts can be interpreted in the following way. After the preparation of the mixtures, some amount of DAT4 remains kinetically entrapped in PS phase, which is demonstrated by its

softening. When temperature is raised above  $T_g$  of PS, mobility of DAT4 molecules becomes sufficient for diffusing into P(S-MI) phase and decreasing free energy of the system in this way.

### FTIR evaluation

DSC results do not give information about MI-DAT interaction, i.e., if the role of DATs consists only in breaking MI-MI hydrogen bonds (inert plasticizer) or new hydrogen bonds between MI and DAT are formed. Such information may be provided by infrared spectroscopy. Before analyzing the spectra obtained from the mixtures, it will be useful to review spectra from polymers and DATs themselves.

Infrared spectra of styrene-MI copolymers with low amount of MI (weight fraction of MI  $\approx$  0.14) were obtained and reported by Vermeesch et al. (see Refs. 11 and 12). Two regions important for the investigation of hydrogen bonding, N—H stretching (3600–3100  $\text{cm}^{-1}$ ) and C=O stretching (1800–1650  $\text{cm}^{-1}$ ), in spectra obtained for the copolymers used in our study are shown in Figures 5(a) and 5(b).



**Figure 5** Infrared spectra of C (—) and BC (·····) in (a) the N—H stretching and (b) the C=O stretching region.

In accordance with interpretation given in above references, a broad band centered at about  $3250\text{ cm}^{-1}$  [Fig. 5(a)] is assigned to a wide distribution of hydrogen bonded structures (multimers) of the MI monomer units. A shoulder apparent at about  $3350\text{ cm}^{-1}$  and a weak band at  $3410\text{ cm}^{-1}$ , respectively, are attributed to hydrogen bonded dimers and free MI units. Comparison of the absorbances of multimer and dimer bands in C and BC leads to a conclusion that MI multimer population is very similar.

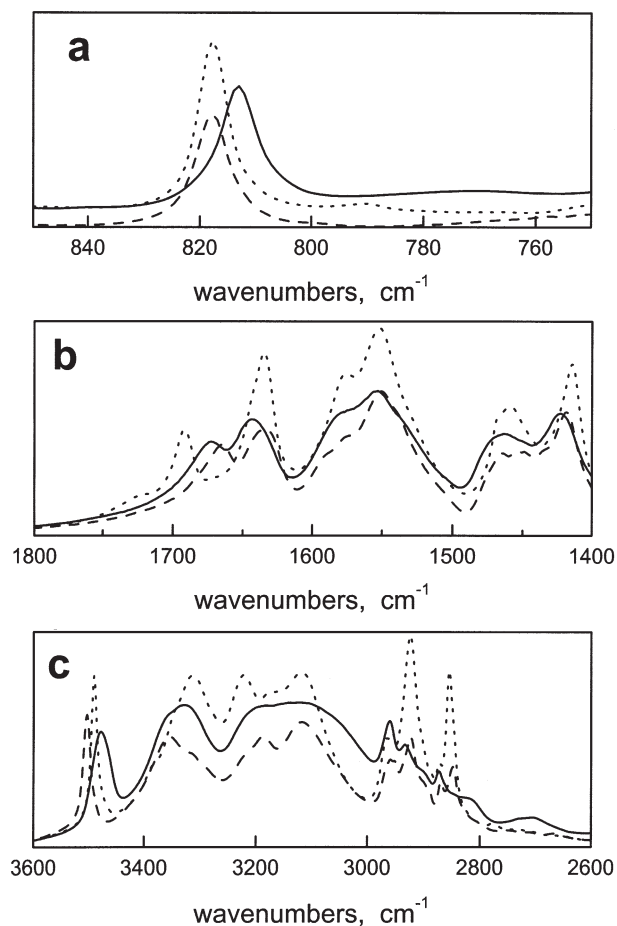
Similarly, two bands shown in Figure 5(b), a smaller one centered at  $1775\text{ cm}^{-1}$  and the round one at ca  $1710\text{ cm}^{-1}$ , respectively, can be attributed to the C=O stretching, which is either in-phase or out-of-phase vibrations with the MI ring. The latter maximum can be deconvoluted into two contributions centered at ca  $1727$  and  $1710\text{ cm}^{-1}$ , which belong to free and hydrogen bonded C=O, respectively. Using the procedure described in Ref. 12, the values of the fractions of free C=O being ca 0.37 (C) and 0.14 (BC), respectively, were obtained. These values are lower than the value 0.67 determined at  $30^\circ\text{C}$  for the styrene-MI copolymer with 14 wt % of MI units by Vermeesch et al.<sup>12</sup>

Spectra of a large series of DATs (including DAT4 and DAT12) were measured and reported by Padgett and Hamner.<sup>24</sup> Three main regions of the infrared absorption,  $850\text{--}750\text{ cm}^{-1}$ ,  $1800\text{--}1400\text{ cm}^{-1}$ , and  $3600\text{--}2600\text{ cm}^{-1}$ , were found. The spectra of DAT4, DAT8, and DAT12 collected by us are shown in Figures 6(a)–6(c).

The single peak in the first region depicted in Figure 6(a) reflects out-of-plane vibrations of triazine ring and is very convenient for the quantitative determination of the content of DAT, since the absorbance of MI and styrene is almost constant here. The position of this peak found for DAT8 and DAT12 ( $818\text{ cm}^{-1}$ ) is shifted only slightly to higher wavenumbers relative to that for DAT4 ( $813\text{ cm}^{-1}$ ).

The second region [Fig. 6(b)] contains doublet assigned to bending of the  $\text{NH}_2$  group. The right peak of the doublet is at ca  $1640\text{ cm}^{-1}$  and does not change significantly with the length of alkyl tail. However, the left peak changes from ca  $1670\text{ cm}^{-1}$  for DAT4 and DAT8 to  $1690\text{ cm}^{-1}$  for DAT12. This mode of  $\text{NH}_2$  vibrations is therefore very sensitive to the changes of structure. At lower wavenumbers, absorption bands originating from the in-plane vibrations of the triazine ring (ca  $1580$ ,  $1555$ ,  $1470$ , and  $1430\text{ cm}^{-1}$ ) are also present.

The third region shown in Figure 6(c) contains absorption bands of asymmetric and symmetric N–H stretching (a few peaks between  $3600\text{--}3000\text{ cm}^{-1}$ ) and C–H stretching (two pairs between  $3000$  and  $2800\text{ cm}^{-1}$ ). A distinct band at ca  $2700\text{ cm}^{-1}$  is seen for DAT4. This band is not discussed in Ref. 24. In accordance with observation made by Vermeesch et al.,<sup>12</sup> this band can be attributed to (amine) N–H... N

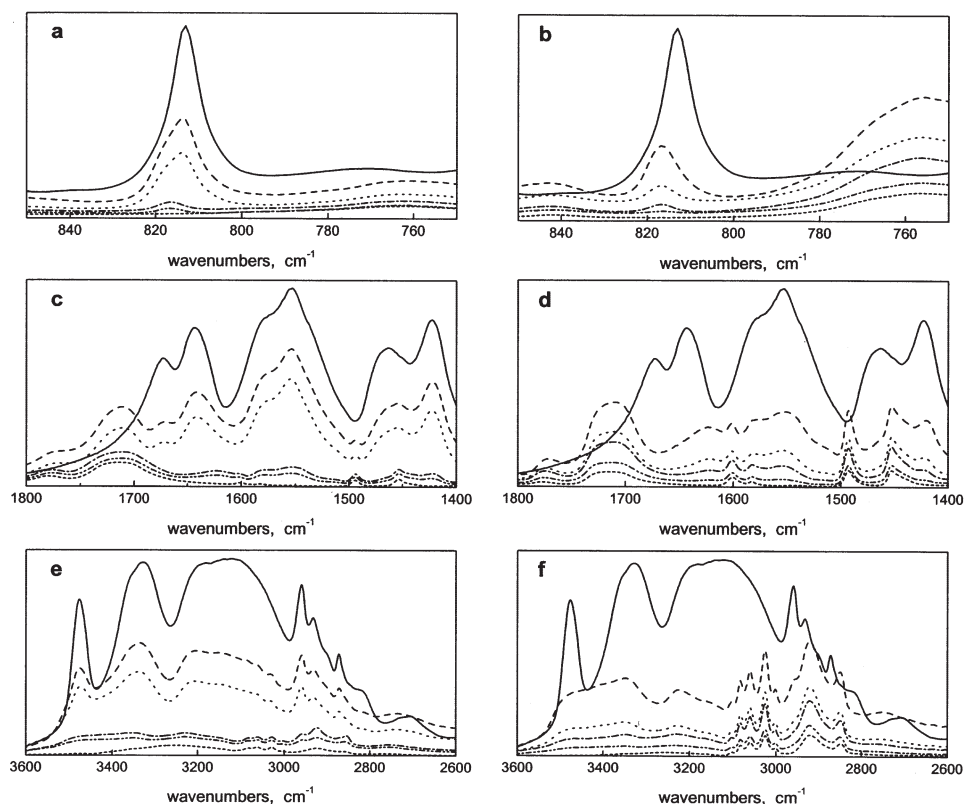


**Figure 6** Infrared spectra of DAT4 (—), DAT8 (---), and DAT12 (· · · · ·) in the regions of (a) out-of-plane triazine ring mode, (b)  $\text{NH}_2$  internal deformations and in-plane triazine ring mode and (c) N–H and C–H stretching.

interassociation of DAT molecules due to hydrogen bonding. The band is less distinct in DAT8 and shifted to higher wavenumbers in DAT12 due to lower concentration of hydrogen bonds.

In the case of MI-DAT interaction, new types of hydrogen bonding not present in MI or DAT themselves (see Scheme 1) may be manifested in the spectra of the mixtures. However, to differentiate bands of new (amine) N–H... O=C from (imide) N–H... O=C and new (imide) N–H... N from (amine) N–H... N, respectively, is a very difficult task.

Spectra obtained for the mixtures of C and BC with DAT4 are shown in Figures 7(a)–7(e). The spectra are complex, nevertheless, a few conclusions can be made. First of all, the out-of plane vibrations of the triazine ring ( $813\text{ cm}^{-1}$ ) are almost unchanged by the presence of MI, both in C [Fig. 7(a)] and BC mixtures (Fig. 7 days). The shift of the band to higher wavenumbers is only  $2\text{ cm}^{-1}$  due to the large mass of the vibrating structure. The band found for C-DAT4 (1:1) and (1:0.5) mixtures consists of two contributions, one being from



**Figure 7** Infrared spectra of the C+DAT4 and BC+DAT4 mixtures in (a)+(d) the out-of-plane triazine mode region, (b)+(e) the  $\text{NH}_2$  bending and in-plane triazine ring mode region, and (c)+(f) the N—H and C—H stretching mode region. Symbols are (—) DAT4, (---) [MI]:[DAT4] = 1:1, (-·-·-) [MI]:[DAT4] = 1:0.5, (·-·-·-) [MI]:[DAT4] = 1:0.25, (- - - -) [MI]:[DAT4] = 1:0.1, (·····) C or BC.

macrophase separated DAT4 and the other from DAT4 dissolved in polymer phase, in agreement with DSC observation. The positions of the band in the BC mixtures correspond to those found for DAT4 dissolved in C-DAT4 mixtures.

Similarly, the positions of the in-plane triazine ring and C=O stretching vibration bands found for the mixtures are almost not influenced by the presence of DAT4 [see Figs. 7(b) and 7(e)] due to the same reason, i.e., the large mass of the vibrating structure. However, the doublet observed in DAT4 at 1640 and 1670  $\text{cm}^{-1}$ , which is attributed to  $\text{NH}_2$  bending, is in the mixtures converted into one wide band and shifted to lower frequencies. This is better seen in BC-DAT4 mixtures, where the band is centered at ca 1620  $\text{cm}^{-1}$ . Contribution from the macrophase separated DAT4 in the C-AT4 mixtures with higher content of DAT4 ([MI]:[DAT4] = 1:1 and 1:0.5) can also be noticed. We think that this observation can be interpreted as an indication of the participation of  $\text{NH}_2$  groups from DAT in a new type of hydrogen-bonding occurring in mixtures.

Unfortunately, because of the complexity of spectra in N—H stretching region, it is not possible to draw conclusions about the changes in population of mul-

timers of MI units. However, a band at ca 2750  $\text{cm}^{-1}$  assigned to N—H...N interassociation of DAT and MI units is again clearly seen in the spectra of mixtures shown in Figures 7(c) and 7(f).

## CONCLUSIONS

Poly(styrene-*co*-MI) precursor and poly(styrene-*co*-MI)-*block*-polystyrene of low polydispersity have been prepared by quasiling radical polymerization. A series of the DAT derivatives with the sites specific for complementary hydrogen bonding to MI moieties has been synthesized. Mixtures of the copolymers with DATs were prepared from the dioxane solutions by evaporation of the solvent.

After the preparation of the mixtures of DATs with copolymer precursor, DATs are dissolved in polymer phase as reflected in decrease of the glass transition temperature, however, at higher contents of DATs a part of them remains macrophase separated in the form of tiny crystallites. Subsequent heating to the temperature higher than the glass transition temperature of the copolymer leads to the dissolving of the crystallites in the polymer phase.



Microphase separated structure of the block copolymer has been confirmed by DSC. After the preparation of the mixtures of DATs with block copolymer, part of low molecular weight compound remains kinetically entrapped in polystyrene phase. Subsequent heating of the mixtures to the temperature higher than glass transition temperature of polystyrene increases the content of DAT dissolved in the poly(styrene-*co*-MI) phase.

Formation of hydrogen bonds between DAT and MI units has been confirmed by FTIR.

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