Blends of tribromostyrene copolymers

J.H. Chu, H.K. Tilakaratne[1], D.R. Paul[*]

Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, USA

Abstract

Copolymers of tribromostyrene (TBS) with styrene (S) and methyl methacrylate (MMA) were synthesized. The miscibility regions for blends of STBS copolymers with the homopolymers polystyrene (PS), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), tetramethyl bisphenol A polycarbonate (TMPC), as well as blends of MMA–TBS copolymers with poly(methyl methacrylate) (PMMA) were determined. Blends of MMA–TBS copolymers with styrene–methyl methacrylate (SMMA) copolymers and blends of both TBS copolymers with styrene–acrylonitrile (SAN) and styrene–maleic anhydride (SMA) copolymers were also investigated. Interaction energies for monomer unit pairs were calculated from the isothermal miscibility maps using the Flory–Huggins theory combined with the binary interaction model. The experimental phase separation temperatures were found to be similar to the spinodal temperatures predicted from the lattice-fluid theory of Sanchez and Lacombe using these interaction energies. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Blends; Tribromostyrene copolymers; Styrene

1. Introduction

Polymers containing halogenated repeat units can yield certain desirable properties [1–3]. For example, Favstritsky et al. [4,5] found that brominated styrene-based monomers copolymerized with conjugated diene monomers exhibit both flame retardancy and good physical properties, as measured by thermogravimetric analysis. It is important to understand the role of such halogens in polymer miscibility for the potential use in commercial applications.

Polymers containing brominated styrene units and their miscibility with other polymers has been studied previously [6–10]; however, most of the attention has been given to mono-brominated styrene polymers. This study investigates the properties of copolymers containing tribromostyrene (TBS) and their blends with both homopolymers and copolymers. Such materials may have interesting properties; for example, it has been suggested that a variety of C–Br bond strengths should be included in an effective flame-retardant [11]. Specifically, copolymers of TBS with styrene (*S*) and methyl methacrylate (MMA) were synthesized and used in blends with the appropriate homopolymer, polystyrene or poly(methyl methacrylate), to determine the interaction energy for the monomer pair.

STBS copolymers were also blended with the homopolymers poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and tetramethyl bisphenol A polycarbonate (TMPC). Blends of these TBS copolymers with styrene–methyl methacrylate (SMMA), styrene–acrylonitrile (SAN), and styrene–maleic anhydride (SMA) copolymers were also investigated. The appropriate interaction energies were determined from the phase behavior data using the Flory–Huggins theory and the binary interaction model.

2. Theory

The general expression for the free energy of mixing is

$$\Delta g_{mix} = \Delta h_{mix} - T\Delta s_{mix} \qquad (1)$$

According to the Flory–Huggins theory [12,13] the free energy of mixing for a blend of polymers A and B is given by

$$\Delta g_{mix} = B\phi_A\phi_B + RT\left[\frac{\rho_A\phi_A \ln \phi_A}{M_A} + \frac{\rho_B\phi_B \ln \phi_B}{M_B}\right] \qquad (2)$$

where R is the universal gas constant, T the absolute temperature, and ϕ_i, ρ_i, and M_i are the volume fraction, density, and molecular weight of component i, respectively. The interaction energy density of a polymer blend, B, can be expressed in terms of interactions between the various pairs of monomer units present and their volume fractions within

* Corresponding author. Tel.: +1-512-471-5238; fax: +1-512-471-7060.
E-mail address: drp@che.utexas.edu (D.R. Paul).
[1] Current address: Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, IA 52242, USA.

Table 1
Forms of the binary interaction model used in this study

Polymer A units	Polymer B units	Equation
1	1 & 2	$B = B_{12}\phi_2''^2$
1	2 & 3	$B = B_{12}\phi_2'' + B_{13}\phi_3'' - B_{23}\phi_2''\phi_3''$
1 & 2	1 & 3	$B = B_{12}(\phi_2'^2 - \phi_2'\phi_3') + B_{13}(\phi_3''^2 - \phi_2'\phi_3'') + B_{23}\phi_2'\phi_3''$
1 & 2	3 & 4	$B = B_{13}\phi_1'\phi_3'' + B_{14}\phi_1'\phi_4'' + B_{23}\phi_2'\phi_3'' + B_{24}\phi_2'\phi_4'' - B_{12}\phi_1'\phi_2' - B_{34}\phi_3''\phi_4''$

the polymer [14,15]:

$$B = \Sigma\Sigma B_{ij}(\phi_i' - \phi_j'')(\phi_i'' - \phi_j') \tag{3}$$

The forms of this equation that are relevant to this study can be found in Table 1. Differentiation of the Flory–Huggins expression for the free energy of mixing gives the following expression for the interaction energy at the critical condition:

$$B_{crit} = \frac{RT_c}{2}\left[\sqrt{\frac{\rho_A}{(\bar{M}_w)_A}} + \sqrt{\frac{\rho_B}{(\bar{M}_w)_B}}\right]^2 \tag{4}$$

where the entropy and enthalpy of mixing are exactly balanced.

Polymer blends often exhibit phase separation on heating, or lower critical solution temperature (LCST) behavior. The Flory–Huggins theory does not predict LCST behavior unless the interaction energy is modified to be temperature dependent. This modification accounts for behavior due to polymer compressibility and possibly other causes.
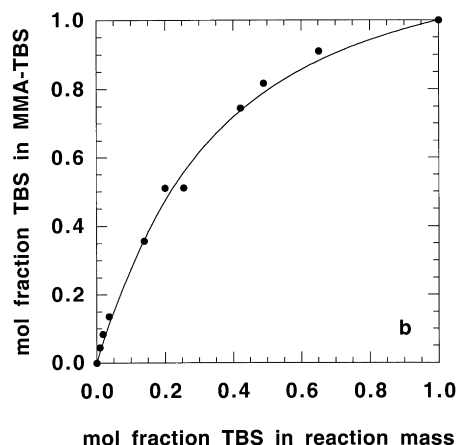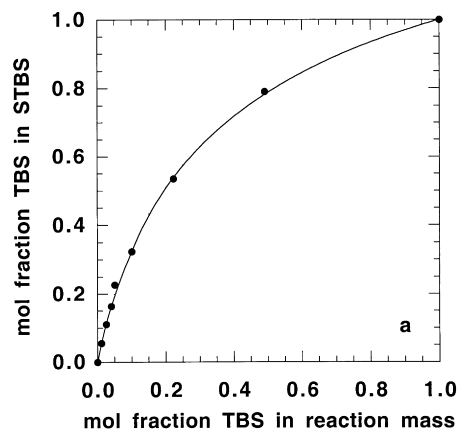

Fig. 1. Copolymer versus reaction mass composition for the free radical polymerization in toluene of tribromostyrene with (a) styrene and (b) methyl methacrylate. The curves represent fits to the data from which reactivity ratios given in the text were determined.

Table 2
Tribromostyrene copolymers synthesized for this study

Abbreviation	wt% TBS	$\bar{M}_n$	$\bar{M}_w$	T_g (°C)	Density (g/cm^3)
STBS 16	16.0	17,600	29,100	105	1.1567
STBS 29	28.6	14,500	24,000	107	1.2470
STBS 39	38.8	14,100	24,200	111	1.3281
STBS 49	48.8	16,300	31,000	114	–
STBS 61	60.8	23,300	37,600	126	1.5493
STBS 79	78.7	45,600	69,100	132	1.7404
STBS 92	92.5	85,200	122,100	133	–
MMA–TBS 4	4.50	67,800	114,800	107	1.2008
MMA–TBS 8	8.39	90,000	137,600	108	1.2159
MMA–TBS 14	13.6	91,500	143,200	109	1.2443
MMA–TBS 20	20.1	89,300	136,000	108	1.2816
MMA–TBS 36	35.7	77,600	123,700	111	1.4132
MMA–TBS 51	51.1	60,900	98,900	121	1.5600
MMA–TBS 61	61.1	81,700	123,100	126	1.6339
MMA–TBS 74	74.5	116,200	179,200	129	1.7296
MMA–TBS 82	81.7	70,600	130,200	126	1.8612
MMA–TBS 91	91.0	137,400	230,400	130	>1.956
PTBS	100.0	173,300	300,500	135	2.0

Table 3
Styrenic polymers used in this study

Polymer	wt% AN or MA or MMa	$\bar{M}_n$	$\bar{M}_w$	Source
PS	0	100,000	330,000	Cosden Oil and Chem. Co.
SMMA4.5	4.5	89,700	186,900	Synthesized
SMMA9	9.0	44,000	96,000	Synthesized
SMMA20.5	20.5	120,000	270,000	Richardson Polymer NOAN 81
SMMA32.5	32.5	80,000	190,000	Synthesized
SMMA38.5	38.5	67,000	130,000	Synthesized
SMMA49.7	49.7	103,600	277,300	Synthesized
SMMA60	58.5	120,000	240,000	Richardson Polymer RPC 100
SMMA70.9	70.9	84,900	127,900	Synthesized
SMMA78.5	78.5	73,900	119,800	Synthesized
SMMA86	86	247,700	1,000,000	Synthesized
SMMA93	93	145,900	608,300	Synthesized
SAN3.8	3.8	93,000	204,000	Asahi chemical
SAN6.3	6.3	121,000	343,000	Dow Chemical Co.
SAN10	10.0	94,700	195,600	Asahi Chemical
SAN12.9	12.9	68,300	151,400	Asahi Chemical
SAN15.2	15.2	56,300	149,000	Asahi Chemical
SAN20.8	20.8	84,300	178,700	Asahi Chemical
SAN25	25	77,000	152,000	Dow Chemical Co.
SAN28.4	28.4	52,900	143,800	Asahi Chemical
SAN30	30	81,000	168,000	Dow Chemical Co.
SAN33	33	68,000	146,000	Monsanto Co.
SAN34	34	73,000	145,000	Asahi Chemical
SAN40	40	61,000	122,000	Asahi Chemical
SMA4.7	4.7	94,000	179,000	Draw Chemical Co.
SMA8	8	100,000	200,000	Arco Chemical Co.
SMA10.1	10.1	62,800	197,300	Dow Chemical Co.
SMA18.1	18.1	92,000	260,000	Dow Chemical Co.
SMA25	25	69,700	252,000	Monsanto Co.
SMA27.9	27.9	76,500	292,100	Dow Chemical Co.
SMA33	33	–	–	Scientific Polymer Products
SMA47	47	–	–	Dow Chemical Co.

Equation-of-state theories, on the other hand, naturally account for compressibility and do predict LCST behavior. One such theory is the lattice-fluid theory proposed by Sanchez and Lacombe [16–20]. The lattice-fluid equations are expressed in terms of characteristic parameters, calculated by fitting experimental PVT data of the polymers. These characteristic parameters can be used to calculate the bare interaction energy ΔP^*, which can be quantitatively related to the Flory–Huggins interaction energy B.

3. Materials and procedures

2,4,5-Tribromostyrene (TBS) monomer, supplied courtesy of AmeriBrom Inc., was purified by recrystallization. A saturated solution of TBS in dichloromethane was filtered and the monomer was collected by precipitation in an acetone/dry ice mixture. This procedure was performed twice. Purity was checked by gas chromatography and melting point (63.8°C). Methyl methacrylate (MMA) monomer was washed with an aqueous sodium hydroxide solution, rinsed with distilled water, and dried over calcium chloride. Styrene (S) and ethyl acrylate was used as-received. Copolymers of TBS with S and MMA were

synthesized in dioxane at 60°C with AIBN as the initiator. A small amount of ethyl acrylate was added to the monomer feed mixtures of the MMA–TBS copolymers to prevent unzipping. Polymer was recovered using an excess of methanol and was purified using dioxane/methanol reprecipitation. Conversion was kept less than 10% to minimize composition drift in the copolymer.

The TBS polymers synthesized in this study are described in Table 2. The comonomer contents of the synthesized polymers were calculated from the bromine content obtained from elemental analysis by Galbraith Laboratories. Fig. 1a shows a plot of copolymer composition vs. reaction mass composition for TBS (1) and S(2). The calculated reactivity ratios are $r_1 = 3.46$ and $r_2 = 0.20$, which are similar to those found by Oishi et al. [21] ($r_1 = 2.78$, $r_2 = 0.23$) for the polymerization performed in toluene. The plot of copolymer composition vs. reaction mass composition for MMA–TBS copolymers is given in Fig. 1b. The reactivity ratios for TBS (1) and MMA (2), not previously reported, were found to be $r_1 = 6.55$ and $r_2 = 0.34$.

Molecular weight information was obtained using gel permeation chromatography calibrated with polystyrene standards. The density of the copolymers was determined at 30°C by a density gradient column using calcium nitrate
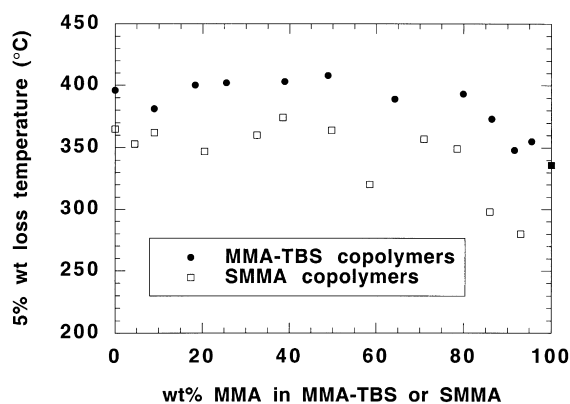
Fig. 2. Temperature of 5 wt% loss versus copolymer composition for MMA–TBS copolymers and SMMA copolymers. For a given MMA composition the MMA–TBS copolymer has a higher 5 wt% loss temperature than its corresponding SMMA copolymer.

and zinc chloride solutions. The accuracy for this technique is generally to the fourth decimal place. The density of the copolymers with large TBS content was determined using zinc chloride solutions with varying densities. An initial solution having a density lower than that of the polymer was made, confirmed by the polymer floating in the solution. A small amount of a solution of higher density was added to increase the density and the solution was mixed to ensure homogeneity. Then, the polymer was placed into the solution again; this procedure was repeated until the polymer sank to the bottom of the solution. This procedure obviously is not as accurate as the density gradient column. The density of PTBS was determined in a similar manner

Table 4
Monodisperse polymer standards used in this study

| Polymer	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Source
PS 680	680	1.16	Polymer Laboratories
PS 800	800	1.3	Pressure Chemical
PS 1350	1350	1.07	Polymer Laboratories
PS 2000	2000	1.06	Pressure Chemical
PS 4000	4000	<1.06	Pressure Chemical
PS 7000	7000	1.03	Polymer Laboratories
PS 9000	9000	<1.06	Pressure Chemical
PS 9860	9860	1.02	Polymer Laboratories
PS 12,900	12,900	1.02	Polymer Laboratories
PS 17,500	17,500	1.04	Pressure Chemical
PS 35,000	35,000	<1.06	Pressure Chemical
PMMA 1400	1400	1.16	Polymer Laboratories
PMMA 2400	2400	1.08	Polymer Laboratories
PMMA 2680	2680	1.09	Polymer Laboratories
PMMA 4250	4250	1.07	Polymer Laboratories
PMMA 5720	5720	1.06	Polymer Laboratories
PMMA10,500	10,500	1.11	Polymer Laboratories
PMMA 13,000	13,000	1.03	Polymer Laboratories
PMMA 20,300	20,300	1.11	Polymer Laboratories
PMMA 33,500	33,500	1.07	Polymer Laboratories
PMMA 60,000	60,000	1.07	Polymer Laboratories
PMMA 73,900	73,900	≤1.07	Pressure Chemical
PMMA 265,600	265,600	≤1.14	Pressure Chemical
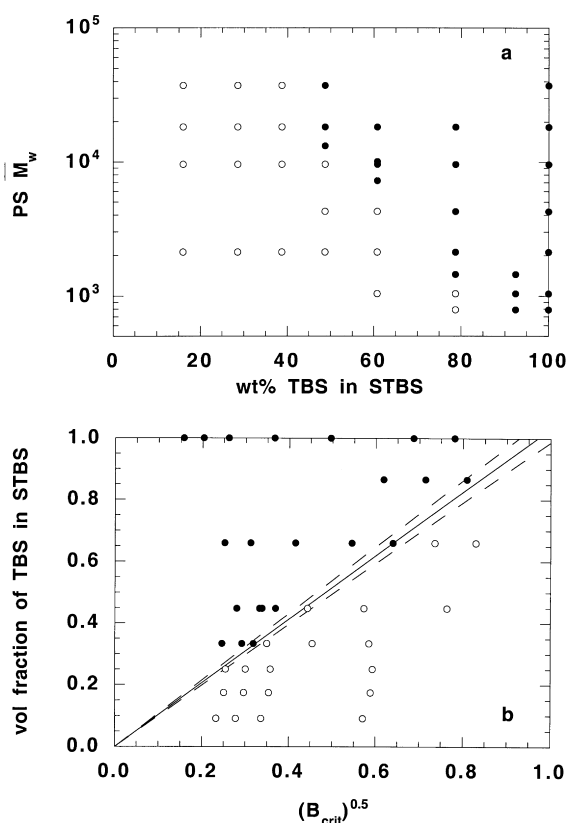
Fig. 3. (a) Isothermal miscibility map at 140°C for 50/50 blends of STBS copolymers with PS homopolymers of varying molecular weights and (b) data replotted according to Eq. (5): (○) miscible; (●) immiscible. Calculations from the slopes of the lines separating the miscible and immiscible blends lead to $B_{S/TBS} = 0.94 \pm 0.08$ cal/cm^3.

using a solution of bromoform and carbon tetrachloride. The value obtained from this method agrees well with the value found by extrapolation of the copolymer densities.

Two SMMA copolymers were also synthesized for this study. The monomers were purified as previously described. The polymerizations were performed at 75°C in bulk using AIBN as the initiator. A small amount (2 wt%) of ethyl acrylate was added to the monomer feed mixtures to prevent unzipping. Polymer was recovered using an excess of methanol and was purified using chloroform/methanol reprecipitation. Conversion was kept less than 10% to minimize composition drift in the copolymer. Information about these and the other styrenic polymers used in this study can be found in Table 3.

A Gnomix PVT apparatus was used to obtain PVT data for PTBS, reported elsewhere [22] from which the characteristic lattice fluid theory equation-of-state parameters were calculated for the temperature range 150–200°C to be $P^* = 572.1$ MPa, $T^* = 814$ K and $\rho^* = 2.090$ g/cm^3. Thermal analysis of the copolymers was performed using a Perkin–Elmer DSC-7 and a Perkin–Elmer TGA-7. A first DSC scan was run to erase thermal history and a second scan was run for analysis, both at scan rates of 20°C/min. TGA runs were also performed at 20°C/min with a nitrogen

purge. Fig. 2 shows the temperature at which 5 wt% loss occurs for the MMA–TBS and SMMA copolymers as a function of wt% MMA. When comparing the copolymers based upon the same MMA content, the MMA–TBS copolymers have a higher 5 wt% loss temperature than the corresponding SMMA copolymer. This shows the copolymer with the brominated styrenic unit has greater thermal stability than the non-brominated polymers and supports the possible use of these polymers in high temperature applications.

Blends were prepared by hot casting from either THF at 60°C or chlorobenzene at 120°C, then dried under vacuum at 140°C for at least 48 h. Phase behavior of blends was determined visually and by DSC, where possible. Phase separation temperatures were determined using a Mettler FP82HT Hot Stage equipped with a Mettler FP80HT Central Processor and DSC. All phase separation observations were checked for reversibility.

4. Blends of TBS copolymers with homopolymers

4.1. Blends of STBS with PS

It is of interest to examine the interaction between tribromostyrene (TBS) and styrene units. One method of doing this is to determine how much TBS can be incorporated into styrene–tribromostyrene (STBS) copolymers and still maintain miscibility with polystyrene (PS). Thus, blends of STBS with monodisperse PS of various molecular weights were cast. Table 4 lists the polymer standards used in this study. Fig. 3a shows the miscibility data for these blends, where open circles represent miscible blends and closed circles represent immiscible blends. At the higher PS molecular weights, the blends were immiscible with STBS copolymers with 48.8 wt% TBS and greater, but at the lowest PS molecular weight of 680, the blends did not become immiscible until the TBS content was 91 wt%.

The applicable form of the binary interaction model is the first equation in Table 1. Since there is only one relevant interaction energy, this provides a method to determine independently the value of $B_{S/TBS}$. Combining Eq. (4) and the first equation in Table 1 leads to:

$$\phi_B = \sqrt{\frac{B_{crit}}{B_{AB}}} \qquad (5)$$

Thus, a plot of the data in the form of ϕ_B versus $\sqrt{B_{crit}}$ can be used to generate a straight line that will separate the miscible and immiscible blends. This line, which passes through the origin, has a slope of $1/\sqrt{B_{AB}}$. Fig. 3b shows the data in Fig. 3a replotted on the appropriate axes, where TBS is the polymer unit B. Also shown is the line separating the miscible region from the immiscible one, along with the region of error encompassed by the dotted lines. The line shown combined with Eq. (5) leads to a value of $B_{S/TBS} = 0.94 \pm 0.08$ cal/cm^3.
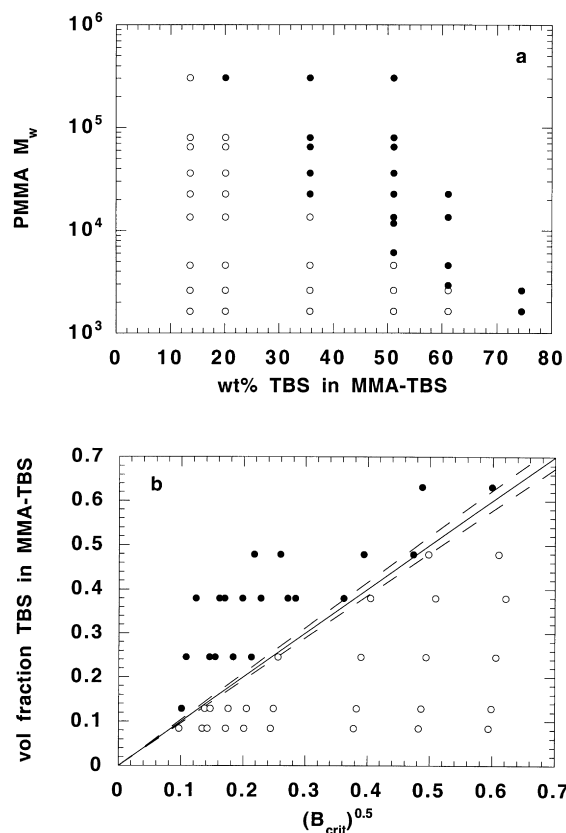

Fig. 4. (a) Isothermal miscibility map at 140°C for 50/50 blends of MMA–TBS copolymers with PMMA homopolymers of varying molecular weights; and (b) data replotted according to Eq. (5): (○) miscible; (●) immiscible. Calculations from the slopes of the lines separating the miscible and immiscible blends lead to $B_{MMA/TBS} = 1.00 \pm 0.09$ cal/cm^3.

4.2. Blends of MMA–TBS with PMMA

Similarly, it is desirable to determine the TBS content in methyl methacrylate–tribromostyrene (MMA–TBS) copolymers necessary to achieve immiscibility in blends with poly(methyl methacrylate) (PMMA) and to isolate the $B_{MMA/TBS}$ interaction energy, so blends of MMA–TBS with monodisperse PMMA of various molecular weight were cast. The raw data are shown in Fig. 4a. MMA–TBS copolymers with less than 13.6 wt% TBS were not used for this analysis, as the determination of miscibility would be difficult due to closeness in both refractive index and glass transition temperature of the polymers. The PMMA standard with the highest molecular weight, $\bar{M}_n = 265,000$, was found to be miscible only with MMA–TBS 14 and was immiscible with all MMA–TBS copolymers with TBS contents of 20.1 wt% and greater. The lower molecular weight PMMA homopolymers were miscible with MMA–TBS copolymers having up to 61.1 wt% TBS.

As in the previous section, the data were replotted in accordance with Eq. (5), see Fig. 4b, in order to calculate the relevant interaction energy. Analysis of the line separating
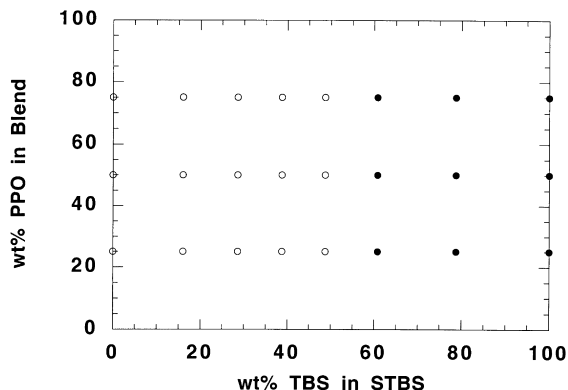
Fig. 5. Isothermal miscibility map at 140°C for 25/75, 50/50, and 75/25 blends of STBS copolymers with PPO: (○) miscible; (●) immiscible. Using $B_{S/TBS} = 0.94$ cal/cm^3 and $B_{S/PPO} = -0.42$ cal/cm^3 gives the estimate of $B_{TBS/PPO} = 1.40 \pm 0.25$ cal/cm^3.

the miscible and immiscible regions gives $B_{MMA/TBS} = 1.00 \pm 0.09$ cal/cm^3.

4.3. Blends of STBS with PPO

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blends with PS are known to be miscible for all compositions. Thus, blends containing PPO and STBS copolymers should exhibit some miscibility at lower TBS contents. STBS copolymers and PPO were blended with the composition ratios 25/75, 50/50, 75/25. PPO was supplied by General Electric Co. ($\bar{M}_n = 29,400$, $M_w = 39,000$) The miscibility map is shown in Fig. 5. Blend miscibility did not change with composition ratio. All blends with STBS copolymers containing up to 48.8 wt% TBS were miscible, while all blends with STBS copolymers containing 60.8 wt% TBS or greater were immiscible. No STBS/PPO blends were found to exhibit LCST or UCST behavior.

As shown by the second equation in Table 1, three interaction energies are required to completely describe the
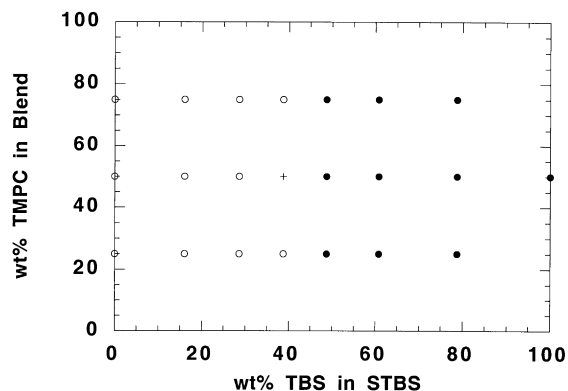

Fig. 6. Isothermal miscibility map at 140°C for 25/75, 50/50, and 75/25 blends of STBS copolymers with TMPC: (○) miscible; (●) immiscible. The blend represented by (+) showed phase separation behavior around 140°C. Using $B_{S/TBS} = 0.94$ cal/cm^3 and $B_{S/TMPC} = -0.02$ cal/cm^3 gives the estimate of $B_{TBS/TMPC} = 1.04 \pm 0.06$ cal/cm^3.

system. Two of the three necessary interaction energies have been defined. The value of $B_{S/TBS} = 0.94$ cal/cm^3 was determined earlier in this study and $B_{S/PPO} = -0.42$ cal/cm^3 has been reported in the literature [7,23–26]. Using these values a range can be determined for the remaining interaction energy, $B_{TBS/PPO}$. The blend of PPO with the STBS copolymer containing 48.8 wt% TBS is miscible which leads to $B_{TBS/PPO} < 1.65$ cal/cm^3. The immiscible blend of PPO with the STBS copolymer having 60.8 wt% TBS gives $B_{TBS/PPO} > 1.16$ cal/cm^3. Assuming the phase boundary lies between these compositions leads to a value of $B_{TBS/PPO} = 1.40 \pm 0.25$ cal/cm^3.

4.4. Blends of STBS with TMPC

Tetramethyl bisphenol A polycarbonate (TMPC) is miscible with PS and is expected to be miscible with STBS copolymers to some degree of bromination. TMPC ($\bar{M}_n = 13,700$, $\bar{M}_w = 37,900$) was provided by Bayer AG. STBS copolymers and TMPC were blended with the composition ratios 25/75, 50/50, 75/25 and the data are given in Fig. 6. All blends with STBS copolymers containing up to 28.6 wt% TBS were miscible, while all blends with STBS copolymers containing 48.8 wt% TBS or greater were immiscible. The 25/75 and 75/25 blends of TMPC with STBS having 38.8 wt% TBS were miscible, but the miscibility of the 50/50 blend was difficult to determine; this point is designated by (+) in Fig. 6. In order to evaluate this blend better, it was re-cast at 130°C. The blend was clearly miscible as cast at 130°C, and phase separated at the original drying temperature of 140°C.

Two of the three necessary interaction energies needed to define the blend system are known. The value of $B_{S/TBS}$ was estimated in a previous section of this study while a value of $B_{S/TMPC} = -0.02$ cal/cm^3 [27] has been reported in the literature, leaving only one interaction energy, $B_{TBS/TMPC}$, to determine. Based upon the LCST behavior of the 50/50 blend of TMPC with the STBS copolymer consisting of 38.8 wt% TBS, the interaction energy is estimated to be $B_{TBS/TMPC} = 1.04 \pm 0.06$ cal/cm^3.

4.5. Effect of bromine on miscibility

Four interaction energies with TBS have been determined thus far: $B_{S/TBS}$, $B_{MMA/TBS}$, $B_{TBS/PPO}$, $B_{TBS/TMPC}$; each of these values is significantly larger than the corresponding interaction energy with styrene, as expected. Kambour et al. [6] studied the miscibility of blends of mono-brominated styrene copolymers with brominated PPO; as a method of comparing the miscibility of these blends, a critical bromination level was defined. This critical bromination level corresponds to the average fraction of repeat units that is brominated in the copolymer with the greatest amount of bromine found to be miscible regardless of the placement of the bromine. The critical bromination level for styrene-*p*-bromostyrene (S-*p*BS)/PPO blends was found to be 0.47. Using their definition, the critical bromination level for
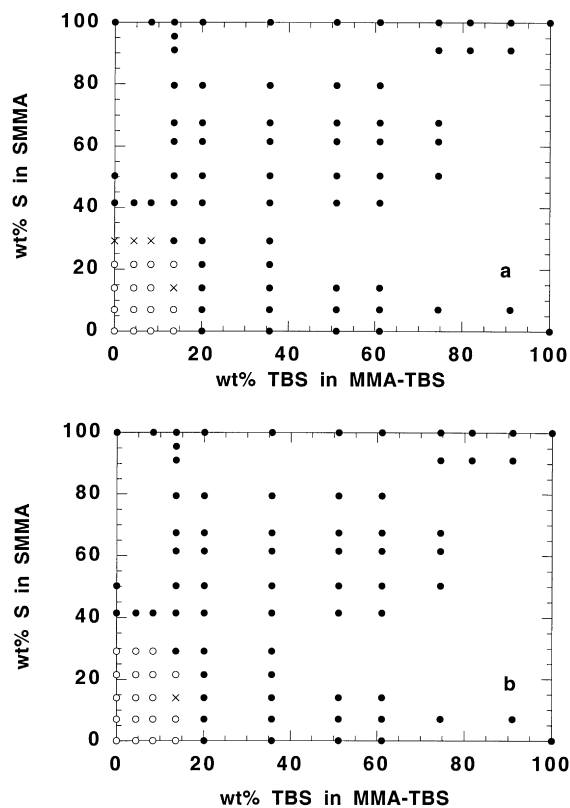
Fig. 7. Isothermal miscibility map at 140°C for 50/50 wt% blends of MMA–TBS copolymers with SMMA copolymers: ($\bigcirc$, $\times$) miscible; ($\bullet$) immiscible. Blends represented by ($\times$) are miscible but predicted to be immiscible using $B_{S/TBS} = 0.94$, $B_{MMA/TBS} = 1.00$, and (a) $B_{S/MMA} = 0.21$ or (b) $B_{S/MMA} = 0.18$ cal/cm^3.

STBS/PPO blends was determined to be 0.22, which is significantly lower.

Another method of comparing these blends based upon degree of bromination is to evaluate the amount of bromine (by weight fraction) in the copolymer, rather than the number of brominated units, with the greatest bromine content found to be miscible. Using this technique, the critical amount of bromine for the S-*p*BS/PPO blends is 0.27, whereas the critical amount of bromine for the STBS/PPO blends is 0.34. These values are much closer, suggesting that the total amount of bromine in the copolymer is a more relevant factor than the number of brominated units for this type of comparison. The critical amount of bromine for the STBS/TMPC blends is 0.27.

5. Blends of TBS copolymers with styrenic copolymers

5.1. Blends of MMA–TBS with SMMA

It is well known that PMMA is miscible with styrene–methyl methacrylate (SMMA) copolymers of low styrene content and that SMMA copolymers containing similar

MMA contents are miscible with each other. Thus, blends of MMA–TBS and SMMA copolymers are expected to exhibit some miscibility. As seen by the relevant equation in Table 1, there are three interaction energies necessary to describe this blend system. The values of $B_{S/TBS} = 0.94$ cal/cm^3 and $B_{MMA/TBS} = 1.00$ cal/cm^3 were discussed above while a value of $B_{S/MMA} = 0.18 - 0.26$ cal/cm^3 [28–35] has been reported in the literature. Since the values of all three-interaction energies have been studied, the miscibility region determined experimentally can be compared to the region predicted by these interaction energies.

Fig. 7 shows the data for these blends, where the open circles and crosses represent miscible blends, while closed circles represent immiscible blends, as determined experimentally. The data along the PMMA/SMMA axis agree with those found previously [36,37]. All blends with SMMA copolymers containing 41.5 wt% S or more were immiscible, as well as all blends with MMA–TBS copolymers containing 20.1 wt% or more of TBS. No phase separation on heating or cooling was observed for these blends.

With a complete set of interaction energies, the experimental data can be analyzed by determining the predicted state of miscibility for each blend using Eqs. (3) and (4). These results can then be used for a direct comparison with the experimental results. In order to compare the data with the estimated interaction energies, the appropriate value of $B_{S/MMA}$ must be chosen. The value of $B_{S/MMA}$ for the temperature of 140°C used in this study is thought to be 0.21 cal/cm^3 [38]. Using this value of $B_{S/MMA}$ to predict the miscibility of these blends leads to agreement with the experimental results with all blends except the few represented by crosses in Fig. 7a, which were found to be miscible but were calculated to be immiscible. By using $B_{S/MMA} = 0.18$ cal/cm^3, the predicted miscibility region is in much better agreement with the experimental data, as seen in Fig. 7b; however this value for $B_{S/MMA}$ was determined at 30°C, which is much lower than the drying temperature here, and all other values of this interaction energy determined at higher temperatures have been correspondingly higher. Another possible explanation for the discrepancies involves the refractive index differences between the copolymers of these blends. Using the method described by Bicerno [39], the refractive index of PTBS was estimated and used to calculate the refractive indices of the MMA–TBS copolymers. The differences in refractive index for the copolymers of the blends in question range from 0.012 to 0.029. While these values are larger than the 0.01 generally used as the minimum difference necessary for accurate visual assessment of whether a blend is homogenous or phase separated, some of these values are close to the minimum and it is possible that the difference in refractive indices may lead to an incorrect visual assessment of miscibility for these blends. Unfortunately, DSC cannot be used for confirmation of miscibility for these blends due to the
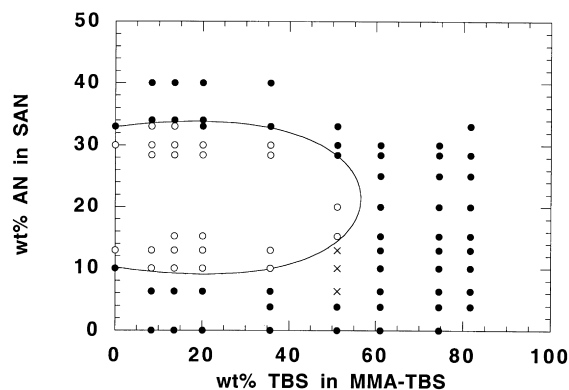
Fig. 8. Isothermal miscibility map at 140°C for 50/50 wt% blends of MMA–TBS copolymers with SAN copolymers: (○) miscible; (●) immiscible. Blends represented by (×) are discussed in the text. The solid curve was calculated from the B_{ij} set obtained from the best fit of the miscibility map: $B_{MMA/TBS} = 1.00$; $B_{S/MMA} = 0.21$; $B_{MMA/AN} = 4.50$; $B_{S/TBS} = 0.94$; $B_{TBS/AN} = 5.34$; and $B_{S/AN} = 7.08$ cal/cm^3.

closeness of their glass transition temperatures. The value of $B_{S/MMA} = 0.21$ cal/cm^3 has been used in the rest of this study.

5.2. Blends of MMA–TBS with SAN

PMMA has a well-defined window of miscibility with styrene–acrylonitrile (SAN) copolymers between AN contents of 12.9 and 30 wt%. Therefore, MMA–TBS copolymers should display some miscibility with SAN copolymers. Fig. 8 shows the data for these blends, where the open circles represent miscible blends, and closed circles represent immiscible blends as determined experimentally. The three blends designated with crosses, all containing MMA–TBS 51, will be discussed in the following paragraph. The addition of TBS to the MMA polymer initially opens the range of miscibility slightly to include SAN copolymers between 10 and 33 wt%, then the range decreases gradually and eventually closes off. The miscibility region of MMA–TBS/SAN differs from the miscibility region of SMMA/SAN [40,41], even though they both have the same borders along the PMMA/SAN axis. All compositions of SMMA exhibit miscibility with some composition of SAN, whereas all MMA–TBS copolymers

containing greater than 61.1 wt% TBS are immiscible with all SAN copolymers.

The state of miscibility for three MMA–TBS 51/SAN blends was difficult to assess. Table 5 contains information used to evaluate miscibility for all MMA–TBS 51/SAN blends in this study, which will be discussed here. The refractive index differences for the three blends with SAN containing 28.4 wt% or more of AN are large enough for visual assessment of blend miscibility. The cloudy visual appearance of these blends as well as the presence of two glass transition temperatures (T_g) in the DSC scans indicate these blends are immiscible. However, all the remaining blends appeared clear. The visual appearance of the blend of MMA–TBS 51 with SAN 3.8 could not be used to determine miscibility due to the small refractive index difference between these copolymers; however, the DSC scan clearly showed two glass transition temperatures corresponding to those of the two pure copolymers, indicating an immiscible blend. The refractive index difference between the copolymers for the blends of MMA–TBS 51 with SAN 20.8 and SAN 15.2 are close to the value generally needed to determine miscibility visually. The DSC results support the visual assessment of miscibility for these blends; one T_g was seen and the breadth of each transition is less than the difference in glass transition temperatures between the corresponding copolymers. This leaves the three blends of MMA–TBS 51 with SAN 12.9, SAN 10, and SAN 6.3. While all three appear clear to the eye, the differences in refractive index between the copolymers in the blends are too small to use visual assessment of whether the blends are homogeneous or phase separated. Unfortunately, the DSC scans for these blends do not provide definitive information. Only one distinguishable T_g is seen for each of these blends; however, the breadth of the transition for each of these blends is larger than the difference in T_g between the component copolymers, leaving open the possibility of two overlapping glass transitions. The breadths of these transitions are also significantly larger than those found for the miscible blends with SAN 20.8 and SAN 15.2; in two of these three blends the transition breadth is more than twice that found for the obviously miscible blends. Although there is not enough evidence for an absolute determination, due to the size of the T_g breadths, these three

Table 5
Properties of MMA–TBS 51/SAN blends

Blend of MMA–TBS 51 with	Visual appearance	Refractive index difference	Number of T_g's	T_g breadth (°C)	$T_{g1} - T_{g2}$ (°C)
SAN33	Cloudy	0.024	2	–	11
SAN30	Cloudy	0.021	2	–	12
SAN28.4	Cloudy	0.020	2	–	12
SAN20.8	Clear	0.014	1	9.0	13
SAN15.2	Clear	0.010	1	9.7	14
SAN12.9	Clear	0.008	1	20.7	14
SAN10	Clear	0.006	1	22.0	15
SAN6.3	Clear	0.003	1	16.8	15
SAN3.8	Clear	0.001	2	–	16

Blend (50/50 wt%)	Predicted spinodal temperature (°C)	Experimental phase separation temperature (°C)
MMA–TBS 8/SAN 33	156	160–165
MMA–TBS 14/SAN 33	167	160–165

blends were treated as immiscible for the following analyses.

The last equation in Table 1 containing six interaction energies is appropriate for this blend system. Three of these ($B_{S/TBS}$, $B_{MMA/TBS}$, $B_{S/MMA}$) have been quantified above. Two of the other interaction energies have been reported in the literature: $B_{S/AN} = 6.7 - 8.0$ cal/cm^3 [32–35,42–44] and $B_{MMA/AN} = 4.1 - 4.55$ cal/cm^3 [33,35,38, 42]. This leaves only $B_{TBS/AN}$ to be determined. A computer program, described elsewhere [22], was used to determine the set of interaction energies, as defined by theory and constrained by the previously determined range of possible values, that bestfit the experimental data. This procedure gives the value $B_{TBS/AN} = 5.34 \pm 0.2$ cal/cm^3, which is actually smaller than the $B_{S/AN}$, the related interaction energy with the non-brominated styrene. The curve shown in Fig. 8 is defined by these interaction energies and shows a good fit to the data.

Two MMA–TBS blends with SAN were found to exhibit LCST behavior; the blends and the corresponding phase separation temperatures are listed in Table 6. Using the interaction energies determined from the copolymer miscibility map and the appropriate characteristic parameters with the lattice-fluid theory predicted spinodal temperatures were calculated. These are also given in Table 6. The experimental phase separation temperatures agree well with the predicted spinodal temperatures.

5.3. Blends of MMA–TBS with SMA

Some styrene–maleic anhydride (SMA) copolymers exhibit miscibility with PMMA and are likely to be miscible with some MMA–TBS copolymers. The miscibility map for blends of MMA–TBS copolymers with SMA copolymers is given in Fig. 9. As with the MMA–TBS/SAN blends, the miscibility region is a closed loop and all blends containing 61.1 wt% TBS or greater are immiscible. This differs from the non-brominated copolymers, where all compositions of SMMA exhibit miscibility with some composition of SMA [34,41]. No LCST/UCST behavior was found with any MMA–TBS/SMA blends.

Three of the six interaction energies relevant to this blend system, $B_{S/TBS} = 0.94$, $B_{MMA/TBS} = 1.00$, and $B_{S/MMA} = 0.21$ cal/cm^3, were evaluated above. Other studies have produced information for two other interaction energies, $B_{S/MMA} = 10.6–10.7$ [27,34] and $B_{MMA/MA} = 7.18$ cal/cm^3 [34], leaving only $B_{TBS/MA}$. The procedure discussed in the previous section was used to estimate this value and produce a set of interaction energies to describe the data. The interaction energy was found to be $B_{TBS/MA} = 8.22 \pm 0.1$ cal/cm^3 which again is smaller in value than the corresponding non-brominated interaction energy, $B_{S/MA}$. As

Fig. 10. Isothermal miscibility map at 140°C for 50/50 wt% blends of STBS copolymers with (a) SAN copolymers and (b) SMA copolymers: (○) miscible; (●) immiscible. The solid curve was calculated from the B_{ij} set obtained from other miscibility maps.
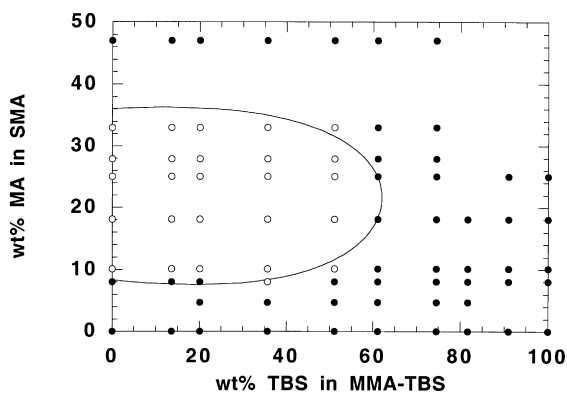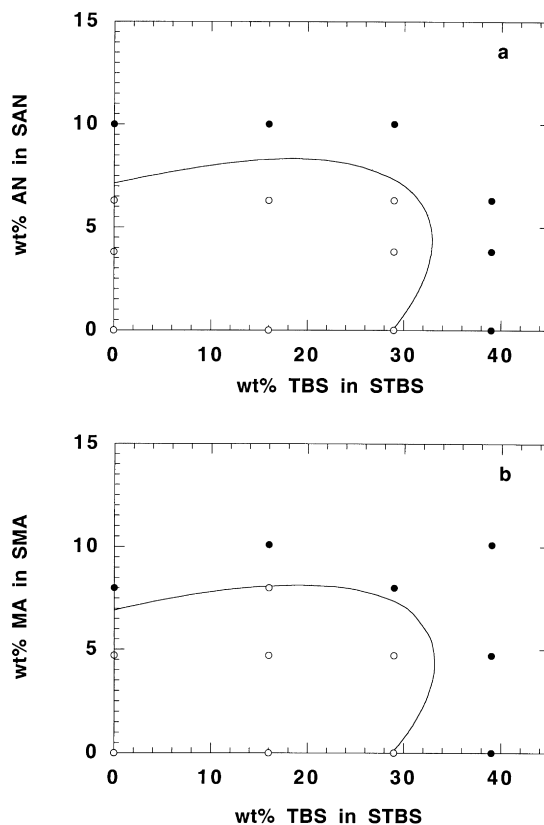
Fig. 9. Isothermal miscibility map at 140°C for 50/50 wt% blends of MMA–TBS copolymers with SMA copolymers: (○) miscible; (●) immiscible. The solid curve was calculated from the B_{ij} set obtained from the best fit of the miscibility map: $B_{MMA/TBS} = 1.00$; $B_{S/MMA} = 0.21$; $B_{MMA/MA} = 7.07$; $B_{S/TBS} = 0.94$; $B_{TBS/MA} = 8.22$; and $B_{S/MA} = 10.66$ cal/cm^3.

Table 7
Interaction energies (B_{ij}, in cal/cm^3) used in this study

j	i			
	Styrene (S)	Confidence limits	Tribromostyrene (TBS)	Confidence limits
S	0	–	0.94	±0.08
MMA	0.21	±0.03	1.00	±0.09
PPO	−0.42	±0.10	1.40	±0.25
TMPC	−0.02	±0.01	1.04	±0.06
AN	7.08	±0.10	5.34	±0.20
MA	10.66	±0.07	8.22	±0.10

demonstrated by the curve in Fig. 9, the interaction energies fit the data fairly well.

5.4. Blends of STBS with styrenic copolymers

Polystyrene homopolymer is miscible with styrenic copolymers, such as SAN or SMA, if the comonomer content is sufficiently low. With the materials in this study, it was possible to evaluate blends of STBS with SAN and SMA, which are expected to have limited miscibility regions. While these blends do not provide additional interaction energy information, they can serve as a further test for those already determined, especially $B_{TBS/AN}$ and $B_{TBS/MA}$. The miscibility maps for these blends are displayed in Fig. 10. The regions of miscibility as predicted by the interaction energies already determined are shown by the curves. The data are indeed consistent with the predictions of the interaction energies.

6. Summary

STBS and MMA–TBS copolymers were synthesized and characterized. The state of miscibility of blends containing these copolymers was used in conjunction with the Flory–Huggins theory and the binary interaction model to calculate interaction energies. The miscibility data for blends of STBS copolymers with PS homopolymers and MMA–TBS copolymers with PMMA homopolymers were used to estimate $B_{S/TBS}$ and $B_{MMA/TBS}$. Additional interaction energy data were determined from the miscibility maps of STBS copolymer with PPO and TMPC homopolymers, and MMA–TBS copolymers with SAN and SMA copolymers. Blends of MMA–TBS copolymers with SMMA copolymers and blends of STBS copolymers with SAN and SMA copolymers produced regions of miscibility consistent with those predicted by the interaction energies determined. All interaction energies determined in this study are positive (see Table 7). It is interesting to note the values of B_{ij} for non-polar units with TBS were greater than the corresponding B_{ij} with S; in some cases, e.g. PPO, the addition of bromine causes the interaction energy to change from negative to positive. However, the values of B_{ij} for polar units, such as AN, with TBS were less than the corresponding B_{ij} with S. STBS/PPO blends were found to have a similar

critical amount of bromine for miscibility as for S-pBS/PPO blends studied elsewhere [6]. Only a few blends were found to exhibit phase separation on heating. The phase separation temperatures were found to be similar to the spinodal temperatures predicted using the lattice-fluid theory and the interaction energies.

Acknowledgements

References

[1] Fire FL. Combustibility of plastics, New York: Van Nostrand Reinhold, 1991.
[2] Troitzsch J. Makromol Chem, Macromol Symp 1993;74:125.
[3] Kharul UK, Kulkarni SS. Macromol Chem Phys 1997;198:1909.
[4] Favstritsky NA, Wang J-L. US Patent 5,066,752, 1991 (Great Lakes Chemical Corporation).
[5] Favstritsky NA, Wang J-L, Rose RS. US Patent 5,100,986, 1992 (Great Lakes Chemical Corporation).
[6] Kambour RP, Bendler JT, Bopp RC. Macromolecules 1983;16:753.
[7] ten Brinke G, Karasz FE, MacKnight WJ. Macromolecules 1983;16:1827.
[8] Vukovic R, Kuresevic V, Ryan CL, Karasz FE, MacKnight WJ. Thermochim Acta 1985;85:383.
[9] Vukovic R, Bogdanic G, Kuresevic V, Srica F, Karasz FE, MacKnight WJ. J Appl Polym Sci 1994;52:1499.
[10] Vukovic R, Bogdanic G, Erceg A, Fles D, Karasz FE, MacKnight WJ. Polymer 1998;39:2847.
[11] Alsheh D, Marom G. J Appl Polym Sci 1978;22:3177.
[12] Flory PJ. J Chem Phys 1942;10:51.
[13] Huggins ML. J Chem Phys 1941;9:440.
[14] Paul DR, Barlow JW. Polymer 1984;25:487.
[15] Paul DR. Pure Appl Chem 1995;67:977.
[16] Lacombe RH, Sanchez IC. J Phys Chem 1976;80:2568.
[17] Sanchez IC, Lacombe RH. J Phys Chem 1976;80:2353.
[18] Sanchez IC, Lacombe RH. Polym Sci, Polym Lett 1977;15:71.
[19] Sanchez IC, Lacombe RH. Macromolecules 1978;11:1145.
[20] Sanchez IC. In: Meyers RA, editor. Encyclopedia of physical science and technology, 11. New York: Academic Press, 1987.
[21] Oishi T, Horie H, Shuyama H. Polym J 1993;25:781.
[22] Chu JH. PhD Dissertation. The University of Texas at Austin, 1999.
[23] ten Brinke G, Rubinstein E, Karasz FE, MacKnight WJ, Vukovic R. J Appl Phys 1984;56:2440.

[24] Maconnachie A, Kambour RP, White DM, Rostami S, Walsh DJ. Macromolecules 1984;17:2645.

[25] Composto RJ, Mayer JW, Kramer EJ, White DM. Phys Rev Lett 1986;57:1312.

[26] Merfeld GD. PhD Dissertation. The University of Texas at Austin, 1998.

[27] Merfeld GD, Paul DR. Polymer 1998;39:1999.

[28] Callaghan TA, Paul DR. Macromolecules 1993;28:2439.

[29] Fukuda T, Inagaki H. Pure Appl Chem. 1983;55:1541.

[30] Fukuda T, Nagata M, Inagaki H. Macromolecules 1984;17:548.

[31] Fukuda T, Nagata M, Inagaki H. Macromolecules 1986;19:1411.

[32] Gan PP, Paul DR. Polymer 1994;35:3513.

[33] Gan PP, Paul DR. Polymer 1994;35:1487.

[34] Gan PP, Paul DR. J Appl Polym Sci 1994;54:317.

[35] Nishimoto M, Takami Y, Tohara A, Kasahara H. Polymer 1995;36:1441.

[36] Feijoo JL, Muller AJ, Acosta JR. J Mater Sci Lett 1986;5:313.

[37] Kohl PR, Seifert AM, Hellmann GP. J Polym Sci, Polym Phys 1990;28:1309.

[38] Chu JH, Paul DR. Polymer 1999;40:2687.

[39] Bicerano J. Prediction of polymer properties, New York: Marcel Dekker, 1993.

[40] Cowie JMG, Lath D. Makromol Chem, Macromol Symp 1988;16:103.

[41] Kammer HW, Kressler J, Kressler B, Scheller D, Kroschwitz H, Schmidt-Naake G. Acta Polym 1989;40:75.

[42] Nishimoto M, Keskkula H, Paul DR. Polymer 1989;30:1279.

[43] Nishimoto M, Keskkula H, Paul DR. Macromolecules 1990;23:3633.

[44] Keitz JD, Barlow JW, Paul DR. J Appl Polym Sci 1984;29:3131.