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Toward a Block-Copolymer-Emulsified, Tough Blend of Isotactic Polystyrene and Polybutadiene: HIiPS

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This report summarizes our efforts to obtain mechanically tough compositions based on the brittle semicrystalline homopolymer isotactic polystyrene. The approach outlined in the report includes the anionic synthesis of isotactic polystyrene (iPS) and diblock copolymers of iPS and polybutadiene (PB) rubber. The diblocks were successful in emulsifying pools of rubber in blends of iPS and PB. A micromechanical toughness test was developed and used to demonstrate the dramatically enhanced toughness of the emulsified blends over the toughness of either the iPS homopolymer or of binary blends of iPS and PB.

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I INTRODUCTION

1.1 Motivation

There has been a tremendous growth recently in the number of novel applications for polymers in a variety of fields such as toughened thermoplastics, highly oriented fibers, gas separation membranes, and electronics related materials as well. The main thrust of the ever increasing number of research projects in these areas can be classified into two main efforts. On the one hand, new chemistries are continuously being explored in an attempt to tailor-make polymers with very specific properties for well defined applications. The second approach instead focuses on attempts to combine the properties of known, well characterized polymers, and it is in this spirit that this work is based.

This combination of existing properties can be achieved by the simple blending of two homopolymers and can at times result in commercially important materials; new miscible combinations are continuosly being explored and comprehensive reviews can be found in the literature[1, 2]. Most polymer pairs however are found to be incompatible and to macroscopically phase separate into domains on the order of hundreds of microns. A lack of interfacial adhesion between these separated phases is reflected in very poor mechanical properties, in general significantly worse than those of the original individual homopolymers. Interpenetrating networks and copolymerization of different monomers present some alternatives to blending, but these techniques often result in a loss of the characteristic properties for which the original materials were chosen.

An alternate possibility involves the use of block copolymers, where large segments of incompatible A and B homopolymers are linked together to form diblock, triblock, star or graft copolymers. The chemical bond restriction limits the thermodynamically driven phase separation to a microscopic scale of a few hundred angstroms. Accurate synthesis procedures allow the targeting of specific block lengths and overall composition which then define the domain size, shape and overall structure of the resulting well defined, thermodynamically stable morphologies. These exhibit a higher degree of interfacial adhesion and a corresponding more effective combination of properties than could otherwise be achieved through simple homopolymer blending. The involved chemistries required to make these materials however is reflected in higher processing costs when compared to the simple and inexpensive method of homopolymer blending.

Experimental work in the area of polymer blends has also shown that for specific cases of non-polar systems, small amounts of block copolymer can act as emulsifiers and break up the macrodomains found in binary blends into a smaller microphase separated morphology, with a high degree of dispersion and much better adhesion between the two phases due to the locating of the blocks in the interface region. A trade-off can then be achieved between the inexpensive but ineffective blend of homopolymers and the beneficial gain in final material properties obtained by the addition of small quantities of more expensive block copolymers.

Recent efforts in this lab have been directed toward the study of semicrystalline block copolymers, as these materials offer a much wider range of possibilities with regards to increased stiffness, resistance to solvents and acids and higher working temperature applications. Along with these advantages come several difficulties from both a synthesis and a processing point of view. The complex chemistries required for the preparation of semicrystalline materials do not usually incorporate themselves well in a diblock preparation scheme, and the degree of interaction between the kinetically driven crystallization and the thermodynamics of phase separation can result in significantly different final structures in the material. The control over microphase separated morphologies that can be obtained using block copolymers in ternary blends represents one attempt at overcoming some of the obstacles presented by semicrystalline materials.

1.2 Objective

The main objective of this work was to examine the emulsifying potential of a semicrystalline diblock copolymer in ternary blends with the respective incompatible homopolymers. The slow and controllable crystallization rate of isotactic polystyrene, available experimental evidence on amorphous PS-PB systems coupled with a parallel study on the deformation mechanisms in homopolymer isotactic polystyrene undertaken in this lab[3] all contributed to the choice of isotactic polystyrene-polybutadiene. This project also presented a unique opportunity to develop a novel means of synthesizing the iPS material and was seen as an opportunity to make a significant contribution in the field of block copolymer anionic polymerization.

The digest will summarize the results of three main efforts that combined to define the bulk of the thesis. First of all, a desciption is given of the basic synthesis procedures for the homopolymers and diblocks, with particular emphasis on the novel low temperature anionic polymerization employed in the preparation of the isotactic polystyrene. The next section addresses the extensive morphology analysis of diblock copolymers samples of varying compositions and subjected to different sample processing techniques in order to characterize the resulting interaction between the thermodynamically driven phase separation and the kinetically controlled crystallization process. Finally, small quantities of semicrystalline diblock copolymers were blended with the respective homopolymers to determine their effectiveness in emulsifying the ternary blend system, especially in the presence of a crystalline phase. Some basic observations are also presented on the relative toughness of the emulsified materials as examined by a newly developed micromechanical toughness analyzer device.

II SYNTHESIS

2.1 Choosing an Appropriate Synthesis Scheme

The selection of polymerization techniques used to prepare the individual isotactic polystyrene and polybutadiene homopolymer blocks was by necessity motivated by the consideration that the chosen methods be also specifically geared for diblock copolymer preparation. One of the most common and effective ways of making these copolymers is by anionic polymerization. This chemistry is of particular interest due to its inherent lack of a spontaneous termination reaction[4, 5]. The active chain ends can then initiate the growth of a second monomer to form multisegmented polymeric materials. Alternatively, the active site can be specially endfunctionalized for subsequent coupling with different blocks. A standard anionic polymerization technique was therefore used to prepare amorphous polybutadiene homopolymers ($T_g \approx -90°C$) with a microstructure of approximately 90% 1,4 and 10% 1,2 addition.

An appropriate polymerization technique for the iPS block was not immediately apparent, as it was necessary to identify a particular chemistry that would allow control over the final microstructure of the material and still be applicable to diblock copolymer synthesis. One of the most common ways of achieving stereospecific placement of vinyl monomer units is by means of a class of heterogeneous metal catalysts known as Ziegler-Natta catalysts. These compounds present a very specific, physically hindering site for incoming monomers, forcing a particular mode of addition preferentially over others. A very extensive review of Ziegler-Natta catalysts and a description of the various factors affecting the choice of metal combinations is available in the literature[6]. A commonly observed result of Ziegler-Natta polymerizations are large molecular weight polydispersities in the final materials (>6) due to the continuous restructuring of the catalytic sites; some chains break off and die while new metal sites develop as the polymerization proceeds. This chemistry cannot be applied to block copolymer synthesis as the terminated chains no longer possess the sought after living chain end characteristic which permits either the growth of a new monomer block or endcapping for a subsequent coupling reaction. It was necessary therefore to identify an alternate synthesis method for iPS.

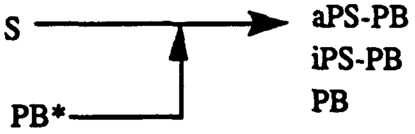
2.2 Anionic Isotactic Polystyrene

Anionic polymerization was first investigated as a possible route for iPS synthesis in order to take advantage of its living chain end characteristic. Though this chemistry generally results in an atactic configuration, where the bulky pendant phenyl ring of the styrene monomer is randomly distributed around the chain backbone, a basic literature review provided evidence that isotacticity, an ordered alternating arrangement of the phenyl groups around the chain, could in fact be induced under certain conditions. In the early 60's partial conversions to isotactic polystyrene were reported for polymerization conditions of low temperatures (≈-30°C), in non-polar solvents, and using linear lithium alkyls as initiators[7-9]. This effect was later attributed to the presence of small quantities of moisture in the reactor setup[10] and interpreted as the reaction of n-BuLi initiator with the moisture in the system to form LiOH, which then associates in some form with the living chain end to provide isotactic placement. This assumption was challenged by investigations in the late 70's which proposed that at very low polymerization temperatures the H_2O molecules associate with the lithium ion to form a complex such as Li(H2O)n+ instead of the hydoxide. The growth of isotactic chains is then attributed to a steric hindrance effect due to the large associating complex. In order to establish some criteria for the purpose of this research, certain fundamental assumptions were agreed upon as a result of this literature review. The basic requirements for isotactic placement to occur were determined to be: 1) a linear alkyl initiator, 2) low temperatures of ≈-30°C, 3) a non-polar medium and 4) some form of associating agent. The actual role of water was unclear at this point, and more work was required in order to be able to make any further assumptions.

An initial series of small scale experiments failed to provide any significant insight into the role of water in the anionic polymerization of styrene, with conversions varying randomly between 0-25% to isotactic product, the remainder being atactic. Rather than pursuing this particular track, an effort was made to identify an alternate compound which could provide the same associating effect attributed to the water-lithium complex without however interfering with the anionic initiator. After reviewing the information found in the literature and after several unsuccessful attempts using compounds such as Bu$_2$Mg and *t*-KOLi, the most encouraging results were achieved using lithium-*tert*-butoxide as the associating agent, with conversions reaching 30% isotactic material[11]. While only a limited amount of work was done to try to optimize this conversion to isotactic product, the identification of a successful anionic polymerization technique for iPS was seen as a significant achievement as it could be applied in a second stage to the preparation of block copolymers.

2.3 Diblock Copolymer Preparation

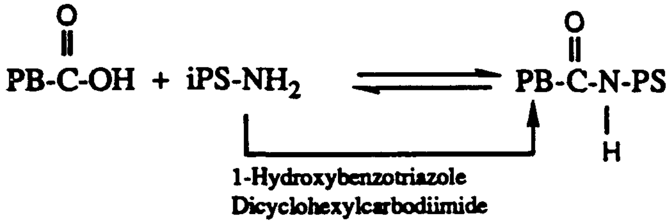
Semicrystalline diblock copolymers of iPS-PB were prepared by one of two methods: 1) sequential polymerization of the two monomers, or 2) termination of the individual homopolymers with specific endfunctionalizers, followed by a coupling reaction to produce a well-defined block copolymer structure. For the sequential polymerization case, living polybutadiene was used to initiate the styrene monomer after the appropriate addition of *t*-BuOLi :



(2.1)

While reactivity data points toward a preferential styrene-first order of addition, the above path was chosen so as to minimize the problems associated with incomplete conversion of styrene monomer associated with the low temerature anionic polymerization technique. Furthermore, the isotactic diblock could be easily extracted from the reaction product by washing in hexane, a solvent for PB and amourphous PS but not isotactic PS.

Coupling presented an opportunity to mix and match different molecular weight polystyrenes and polybutadienes so as to tailor-make diblock copolymers of varying compositions. The chosen coupling reaction for these materials consisted of a condensation between an amine terminated polystyrene and a carboxylic acid endcapped polybutadiene in the presence of coupling agents that shifted the otherwise equilibrium reaction towards complete conversion[12]:



$$\text{PB-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OH} + \text{iPS-NH}_2 \xrightleftharpoons[\substack{\text{1-Hydroxybenzotriazole}\\ \text{Dicyclohexylcarbodiimide}}]{} \text{PB-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-}\underset{\underset{\text{H}}{|}}{\text{N}}\text{-PS} \tag{2.2}$$

2.4 Experimental

Polybutadiene was prepared in a 10% solution in hexane at ≈ 50°C using n-BuLi as the preferred anionic initiator. Some of the polymerizations were terminated by the addition of carbon dioxide gas to provide the -COOH functionality required for the coupling reaction[13]. Characterization of the molecular weight and the degree of tacticity was achieved through GPC and ^{1}H NMR. Results of several polymerizations are listed in Table 2.1.

Isotactic polystyrene material was synthesized in non-polar hexane solvent at ≈-25°C for several days in the presence of a 1:1 n-BuLi/*t*-BuOLi or living PB/*t*-BuOLi initiator to associating agent ratio. Termination was achieved either by the injection of a few ml. of degassed methanol or by the addition of N-(benzylidene)trimethylsilylimine; this resulted in a protected endgroup that could then be converted into an -NH_2 functionality through a simple hydrolysis[14, 15]. After precipitating into cold methanol, the recovered PS product was placed in a Soxhlet extractor cup and the atactic polystyrene removed by refluxing in methyl ethyl ketone. The reflux was left running for several days until the insoluble portion was determined to be >95% isotactic as characterized by ^{13}C NMR spectra: in the range of 140-150 ppm, it is possible to distinguish three peaks at 145.6, 146.0 and 146.8 ppm for syndiotactic, atactic and isotactic polystyrene respectively[16]. The molecular weights of these materials and relevant thermal data were obtained by GPC and DSC. Results of several homopolymer synthesis are summarized in Table 2.2.

For the sequential diblock polymerization, n-BuLi initiated living polybutadiene was added to a flask containing styrene monomer, a hexane/toluene solvent mixture and sufficient *t*-BuOLi to make a 1:1 ratio with the living PB. Reactions were left running at ≈-25°C for several days, after which termination was accomplished by the addition of a few cc. of methanol and the isotactic diblock extracted by repeated washing of the precipitated product in hexane. The PB chain was characterized prior to styrene monomer addition, but the molecular weight of the sequential polystyrene segment had to be inferred from ^{1}H NMR information as it could not be characterized separately from the initial rubber chain. Coupling of the endfunctionalized homopolymers was conducted in dry toluene under inert argon atmosphere conditions to minimize polybutadiene oxidation in the presence of the 1-hydroxybenzotriazole (HOBT) and dicyclohexylcarbodiimide (DCCI) coupling agents. A summary of the polymerization conditions for several diblocks is given in Table 2.3, while characterization results for the same materials are collected in Table 2.4.

2.5 Results of Diblock Synthesis

The anionic polymerization of styrene at low temperatures in the presence of an associating agent has been proven to be an effective method for the preparation of isotactic polystyrene homopolymers. While the present 20-30% conversions to isotactic product are not exactly comparable to those achieved with Ziegler-Natta catalysts (≈95%), the living chain end characteristic of anionic synthesis can be incorporated into an effective scheme for the preparation of semicrystalline iPS/PB diblock copolymers. Some basic observations regarding the kinetics of the reactions could be drawn from available ^{13}C NMR data. Figs. 2.1 and 2.2 represent the ^{13}C spectra for the insoluble and soluble fractions of the total polymerization product as recovered after refluxing for several days in MEK. The sharp peak at 146.8 ppm for the insoluble fraction is interpreted as a higher than 95% isotactic content[16]. The absence of any significant atactic component in this signal indicates that once a chain starts out growing isotactically, it continues to add units in the same manner rather than shift back and forth from the t-BuOLi associated to the non-associated dimeric polystyryl form typical of atactic conversion in the anionic synthesis of styrene at higher temperatures. Thus at lower temperatures the reactor solution is envisioned as consisting of a static mixture of associated complexes, which result in the formation of the iPS fraction of the total product, and unassociated

TABLE 2.1 Characterization results for n-BuLi initiated polybutadiene polymerizations in hexane

Sample	Polym. Temp. °C	%1,4	%1,2	Mn	T_g	Endgroup
PB11	28	89	11	11,000	-91	-COOH
PB4.5	28	90	10	4,500	-95	living*
PB13	50	90	10	13,000	-92	living*
PB4.2	50	91	9	4,200	-94	living*
PB25	50	89	11	25,000	-92	- - -
PB52	50	91	9	52,000	-90	-COOH

* denotes living chain used in a sequential polymerization scheme

TABLE 2.2 Characterization results for the anionic low temperature synthesis of isotactic polystyrene in the presence of *t*-BuOLi

Sample	*t*-BuOLi / n-BuLi	Mn iPS	T_g	T_m	% crystall.	Endgroup
PSO	0	- - -	- - -	- - -	- - -	- - -
iPS18	1.25	18,000	99	204	20	- - -
iPS22	1.00	22,000	100	209	11	- - -
iPS41	0.99	41,000	99	212	12	$-NH_2$
iPS57	1.00	57,000	100	210	21	$-NH_2$
iPS73	0.99	73,000	97	209	3	$-NH_2$
iPS100	1.00	100,000	102	216	12	$-NH_2$

TABLE 2.3 Polymerization Conditions in Hexane

Sample	Block	Polym. Temp. °C	Initiator	Endcapping Agent
S41/B11	PB	50	n-BuLi	CO_2
(coupled)	iPS	-30	n-BuLi/*t*-BuOLi	$C_5H_6CHNSi(CH_3)_3$
S15/B4.5	PB*	50	n-BuLi	not terminated
(sequential)	iPS	-30	PB*/*t*-BuOLi	MeOH
S30/B13	PB#	50	n-BuLi	not terminated
(sequential)	iPS	-30	PB#/*t*-BuOLi	MeOH
S100B52	PB	50	n-BuLi	CO_2
(coupled)	iPS	-30	n-BuLi/*t*-BuOLi	$C_5H_6CHNSi(CH_3)_3$

*,# indicate living polybutadiene used in sequential block polymerization

TABLE 2.4 Diblock Characterization

	S41/B11	S15/B4.5	S30/B13	S100/B52
Wt% iPS	79	77	70	66
Wt% PB	21	23	30	34
Mn iPS	41,000	15,000	30,000	100,000
Mn PB	11,000	4,500	13,000	52,000
T_m iPS °C	210-216	204-210	205-210	213
T_g iPS °C	97	92	92	89
T_g PB °C	-91	---	-92	-88
% cryst. *	11-20	7-11	3-7	20

* Based on DSC measurements and taken on a polybutadiene-free basis

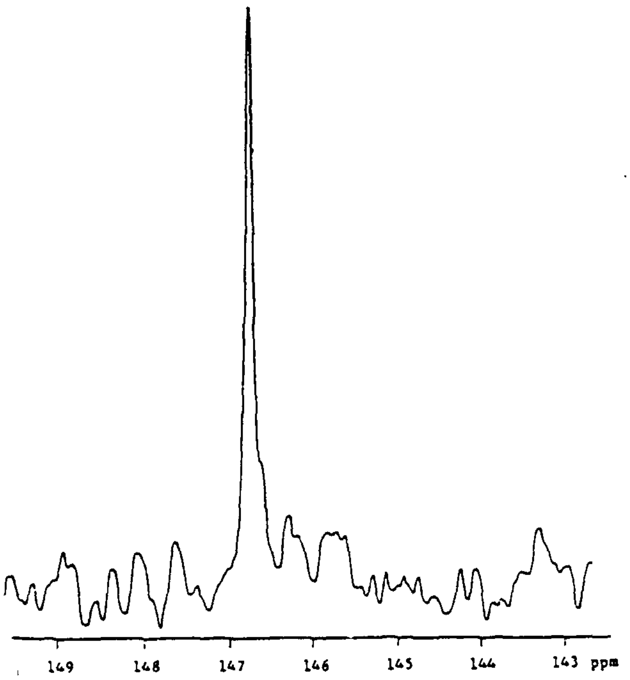


Figure 2.1 ^{13}C NMR spectra of the MEK insoluble fraction of polymerization product

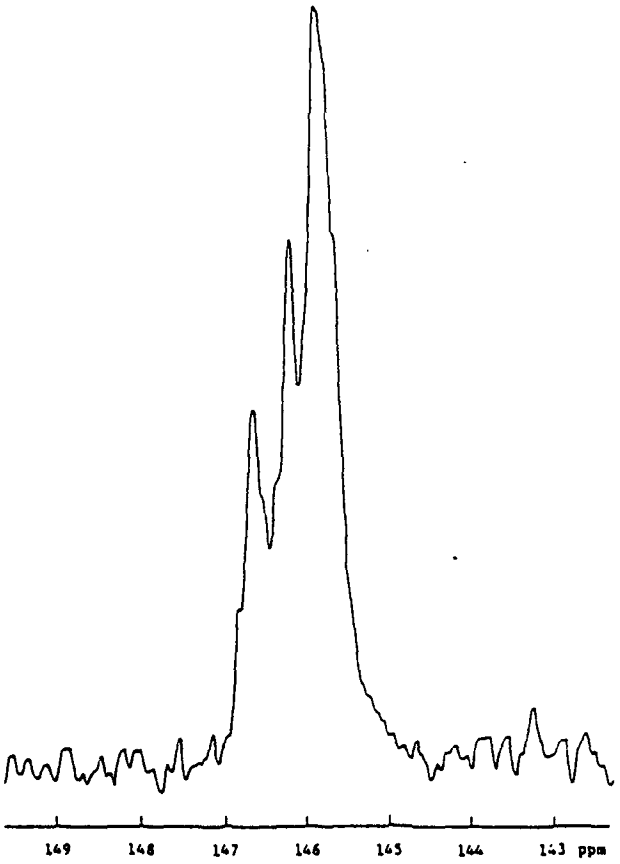
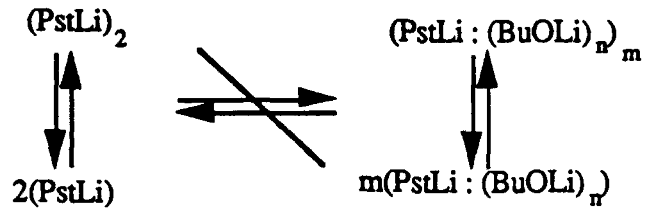


Figure 2.2 ^{13}C NMR spectra of the MEK soluble fraction of polymerization product

anions, yielding the atactic material:



Atactic copolymer material, uncoupled homopolymers and prematurely terminated amorphous PB chains were removed from the final diblock product through a extensive series of extraction and fractionation steps. The final composition was determined though a combination of GPC data and, especially for the sequential diblock, through ^{1}H NMR: the ratio of the styrene aromatic proton peaks (≈7.0 ppm) to those of the polybutadiene (≈4.5-5.0 ppm) and the known Mn of the original PB segment were sufficient to back out an approximate molecular weight for the iPS block. DSC provided further insight regarding the block-like nature of the copolymers. A transition at ≈ 65°C for the smaller S15/B4.5 diblock indicates a homogeneous material with some crystalline domains containing amorphous glassy iPS that accounts for the T_g^{iPS} at 92°C. The remaining copolymers displayed strong transitions at approximately -90°C for T_g^{PB} and a slightly depressed T_g^{iPS} of 92°C (with respect to the homopolymer value of 100°C) that correctly follows the expected trend observed for heterogeneous diblock copolymers of aPS/PB[17].

Transmission electron microscopy (TEM) is a useful tool for characterizing the diblock nature of the synthesized materials. Due to the nature of the chemical linkage between blocks, these materials phase separate into very distinct morphologies on the scale of nanometers. By preferentially staining one phase, visual evidence can be obtained regarding the microstructure of the final material as described in the next section.

III MORPHOLOGY ANALYSIS OF DIBLOCK COPOLYMERS

3.1 Introduction to Phase Separation

Fundamental to any study of multicomponent blend systems is an understanding of the basic thermodynamic principles that govern miscibility. Starting with the simple case of blending of two different homopolymers, the general equation for phase stability derived from the Flory-Huggins liquid lattice model can be written as $\Delta G_m = RT\{(1/V_1)\phi_1 \ln\phi_1 + (1/V_2)\phi_2 \ln\phi_2\} + \Lambda_{12}\phi_1\phi_2$, where the first term accounts for the combinatorial entropy of mixing, while all enthalpic factors are grouped in the last term. Though miscibility is still seen as the exception rather than the rule, the realization that it is governed primarily by the enthalpic interactions between polymers rather than by combinatorial entropic effects has led to the identification and classification of a large number of binary or higher order homogeneous blends[1, 2]. Homogeneity, however, does not always provide the most attractive combination of material properties. Proper control over the degree of phase separation and adhesion in immiscible polymer blends has been noted to result in significant improvements in the mechanical properties of the blend. How to achieve some form of control over the heterogeneity of a system is then a key issue when attempting to reproduce morphologies that result in specific structural properties. Block copolymers offer tremendous possibilities in this respect as the extent of phase separation in these systems is governed primarily by the relative size of the block segments which allows targeting of equilibrium microstructures to fit a variety of applications. Thermodynamic equilibrium however is rarely achieved when working with polymeric materials due to the time scales and/or temperatures associated with the required processing steps. It is then necessary to consider other parameters, be it external or material related kinetic processes such as crystallization, that combine with phase separation to define a final material morphology.

3.2 Phase Separation in Diblock Copolymers

Several theories of note have been proposed over the past 30 years that attempt to define the thermodynamics of diblock copolymer phase separation. The statistical thermodynamics approach first introduced by Meier[18, 19] and later expanded by Helfand and Noolandi[20-25] provides a convenient analytical expression for describing phase equilibria in diblock copolymer systems by "building up" the free energy expression through the addition of appropriate terms based on learned intuition and experience. The main parameters that are included in such derivations are: 1) an interfacial tension term between polymer segments A and B, 2) an entropy loss term due to localization of the junction points to an interface region of dimension a_j, and 3) a loss of conformational entropy term which satisfies a criteria of uniform chain density throughout the domains. Both theory and experimental evidence point toward a critical molecular weight for phase separation in diblock copolymers a factor of approximately 5 to 5.5 higher than that predicted for the corresponding homopolymer blend[26-29].

One of the most attractive characteristics of block copolymers is the control that can be achieved over resulting phase separated equilibrium morphologies. Meier was one of the first investigators to provide theoretical calculations for the stability of different domain morphologies as a function of block molecular weights[26]. As shown in Fig.3.1, the system tends to reduce the effect of chain perturbations arising from differences in the relative molecular weights of the blocks by introducing curvature into the phase separated domains, from lamellae for a symmetrical case to spheres for the extreme of large A and small B. Also included is a newly proposed ordered bicontinuos double-diamond (OBDD) morphological packing order[30-35]. Control over the molecular weight of each block then allows the targeting of well defined morphologies and provides a useful way of engineering polymeric materials for a variety of specific applications. In practice however several factors contribute to make it quite difficult or at times even impossible to prepare samples which display this expected equilibrium phase separation. One must therefore consider not only the thermodynamics of phase separation when discussing the preparation of polymer samples but also other external effects.

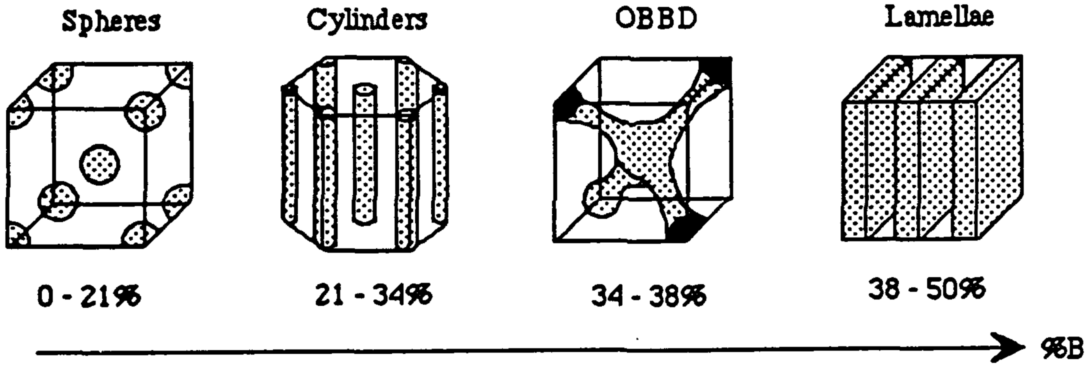


Figure 3.1 Equilibrium morphologies of an A-B diblock copolymer as a function of relative block length B.

3.3 Crystallization

The possibility of incorporating certain characteristics of crystallinity into homopolymer mixtures has become the focus of several investigations in the area of semicrystalline blends. Quite often, this crystallization needs to be incorporated into an existing phase separated morphology in order to take advantage of certain microstructure related properties. It is then critical to be able to control the degree of interaction between the thermodynamically driven equilibrium state provided by phase separation and the kinetic phenomenom of crystallization.

The concept of semicrystalline diblock copolymers has only recently been dealt with in the literature. A variety of parameters such as crystallization temperature, chemical nature of the rubber component, particle distribution and the molding processes involved that can contribute to define a final microstructure make it difficult to accurately predict the equilibrium state of a sample. A few theoretical papers have recently appeared in the literature which describe the system in terms of flexible and folded chains for the amorphous and semicrystalline blocks respectively[36, 37]. Though simplified scaling laws are derived for the expected domain sizes and periodicity, these theories are generally limited to lamellar phase separated morphologies and have not yet been extended to other structures. The small number of theoretical treatments of semicrystalline diblock copolymers is closely matched by the relatively limited amount of experimental work done involving these materials due once again to the complex chemistry invovled. Studies on semicrystalline block copolymer systems such as PEO-PS, PEO-PMMA, PEO-PB and PE-PB[38-42] have focused essentially on the kinetics of crystallization and on the observed effect of the added rubbery component on parameters such as chain folding and domain lamellae thickness. Other approaches make extensive use of transmission electron microscopy, X-ray diffraction and light microscopy data to provide an effective visual representation of the morphological structure in support of phase diagrams proposed to describe the observed interrelation of the crystallization and phase separation binodal curves[43]. This thesis follows this particular approach as the competition between the thermodynamics of phase separation and the kinetics of crystallinity is characterized primarily by transmission electron microscopy under different conditions of molecular weight and processing techniques.

3.4 Results

Four semicrystalline diblock copolymers (Tables 2.3-4) were prepared in the course of this thesis. Only the results pertaining to S15/B4.5 and S30/B13 will be discussed in this digest as these materials are well representative of all structures investigated in the course of this analysis. In order to provide a simple framework in which to examine the iPS-PB diblock copolymers, two extreme cases were considered, that of crystallization occuring prior to or after phase separation. These set of conditions were fulfilled by processing the available diblocks one of two ways:

1) Molding of the precipitated powder between glass slides at T≈ 260°C, allowing the sample to then equilibrate between 2-5 minutes before quickly cooling it down to ambient temperature. Crystallinity was imposed by annealing the material at the optimum crystallization temperature $T_c \approx 175°C$[3] for several hours.

2) The copolymer was dissolved in a 0.5-1.0% solution in toluene and static cast at ≈ 50°C for several days to make films varying between 0.1-0.2 mm in thickness.

Staining of the polybutadiene domains with OsO_4 and the crystalline regions with RuO_4 in ultramicrotomed thin samples (@500 Å) provided sufficient contrast for TEM analysis of the final microphase separated morphology. This information was then used to construct simplified phase diagrams that qualitatively describe the observed phase stability curves for each system.

S15/B4.5 DIBLOCK

Fig.3.2 is a TEM micrograph of S15/B4.5 heated to ≈ 260°C and then quenched so as to reduce effects of crystallinity. No visible phase separation is apparent, indicating that the diblock is homogeneous in the observed temperature range. When the sample is annealed at 175°C for several hours, crystallization of the iPS matrix results in an exclusion of the polybutadiene into separate irregular domains (Fig.3.3). Crystallization under these conditions was found to supress any ordered microphase separation that would otherwise typify a diblock copolymer structure. The same morphology is observed when the same material is static cast from toluene at ≈ 50°C; no distinct isotactic polystyrene-polybutadiene phase separated domains can be identified (Fig.3.4). The low molecular weight diblock is expected to encounter the liquid-solid transition prior to the microphase separation curve regardless of the chosen processing pathway as shown in the simplified phase diagram of Fig.3.5.

S30/B13 DIBLOCK

Fig. 3.6 is a TEM micrograph of the S30/B13 copolymer molded at ≈ 260°C and quickly quenched to ambient temperature. The observed morphology consists of dark O_sO_4 stained spherical

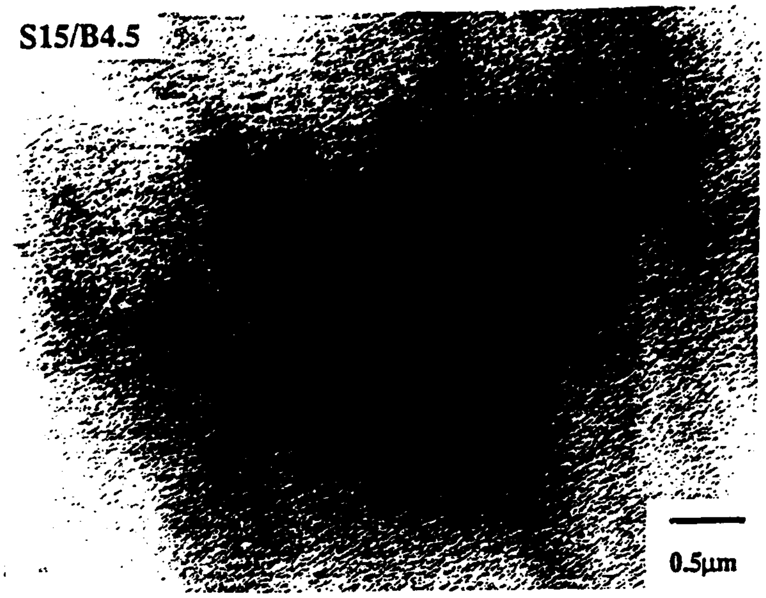


Figure 3.2

TEM micrograph of S15/B4.5 molded at ≈ 260°C and quickly quenched to ambient temperature

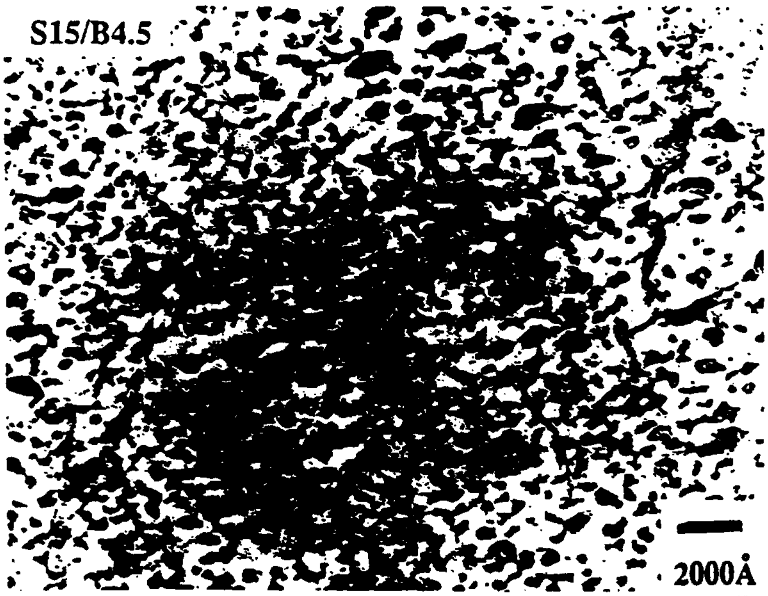


Figure 3.3

TEM micrograph of S15/B4.5 molded at ≈ 260°C and annealed at 175°C for 4 hrs.

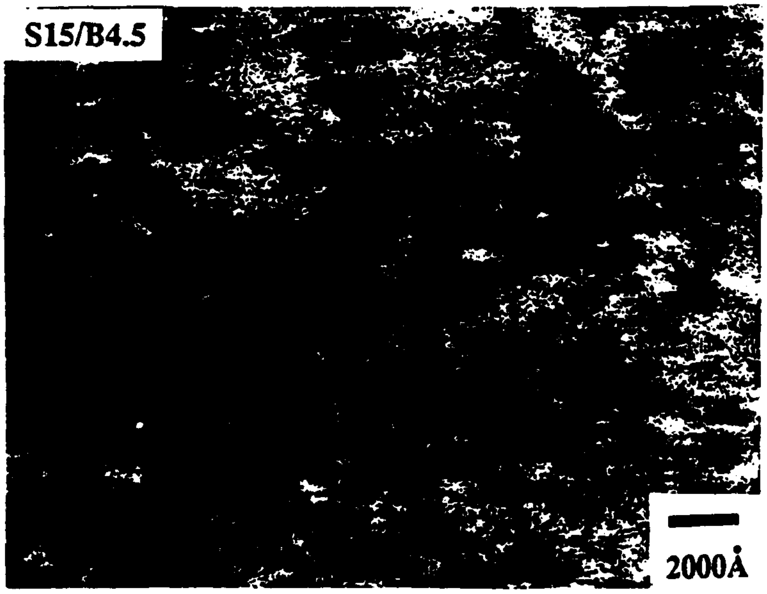


Figure 3.4

TEM micrograph of S15/B4.5 static cast from toluene at ≈ 50°C

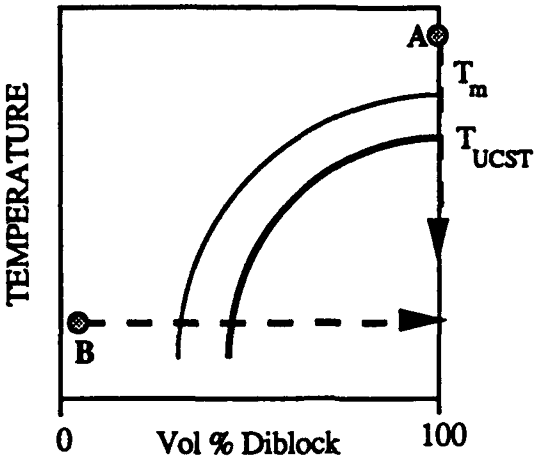


Figure 3.5 Simplified phase diagram for the S15/B4.5 semicrystalline diblock copolymer-solvent system

polybutadiene domains evenly distributed throughout the white isotactic polystyrene matrix. The regularity and scale of this phase separated structure is a strong indication of a successful sequential polymerization. Imposing crystallization on the material at this stage does not appear to significantly affect the observed microphase separated morphology. As seen in the micrographs of Figure 3.7 , the spherical morphology observed in the amorphous sample persists in the crystallized material (Fig. 3.7a) for which evidence of spherulites can also be seen at lower magnifications (Fig. 3.7b). When the formation of spherulitic crystalline texture occurs in the presence of the microphase separated morphology, the former appears to engulf the latter but does not destroy or disrupt the nanoscale structure. Casting the same diblock from solution results in a significantly different morphological structure, as shown in the TEM micrograph of Figure 3.8. The lack of any ordered PB domains indicates that crystallization has proceeded and in effect supressed microphase separation, with the rubber resulting excluded from the crystalline domains. Unlike the previous S15/B4.5 example, different processing methods resulted in different final morphologies for the higher molecular weight S30/B13 diblock. The basic phase behavior of this semicrystalline copolymer can then be schematically described by the simplified phase diagram of Fig.3.9.

These simple phase diagrams are valid only for a specific set of conditions and do not exclusively define the system. Different choice of casting solvent, casting and molding speed can all contribute to shift either the solid-liquid transition or the phase stability curve and result in a

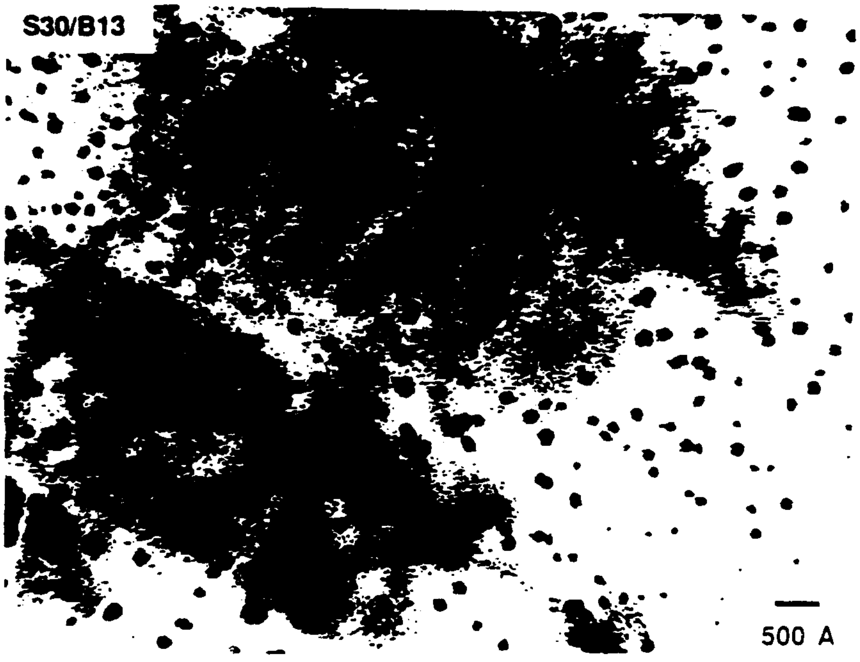


Figure 3.6 TEM micrograph of S30/B13 semicrystlline diblock copolymer, molded at approximately 250°C and quenched to ambient temperature

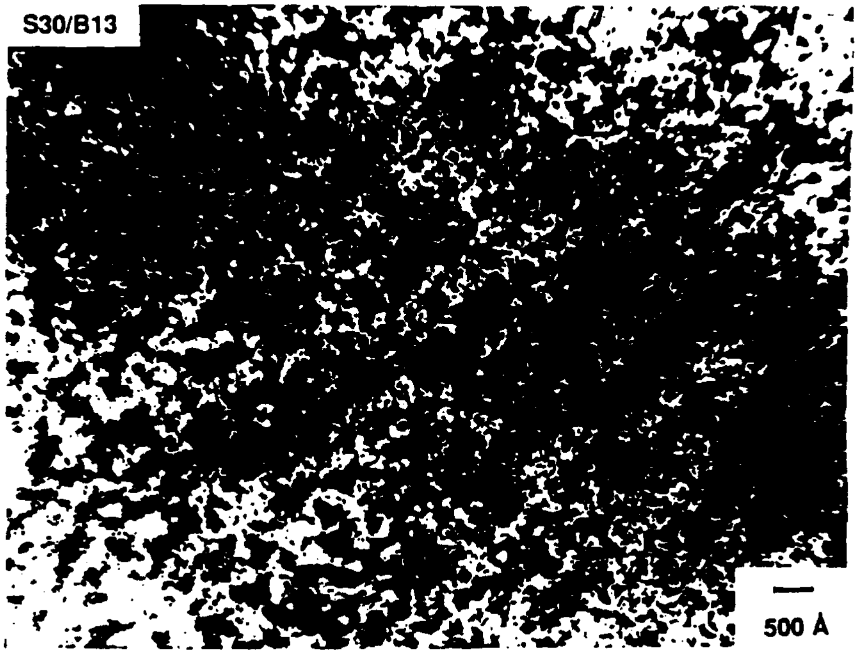


Figure 3.8 TEM micrograph of S30/B13 static cast from toluene at ≈ 50°C.

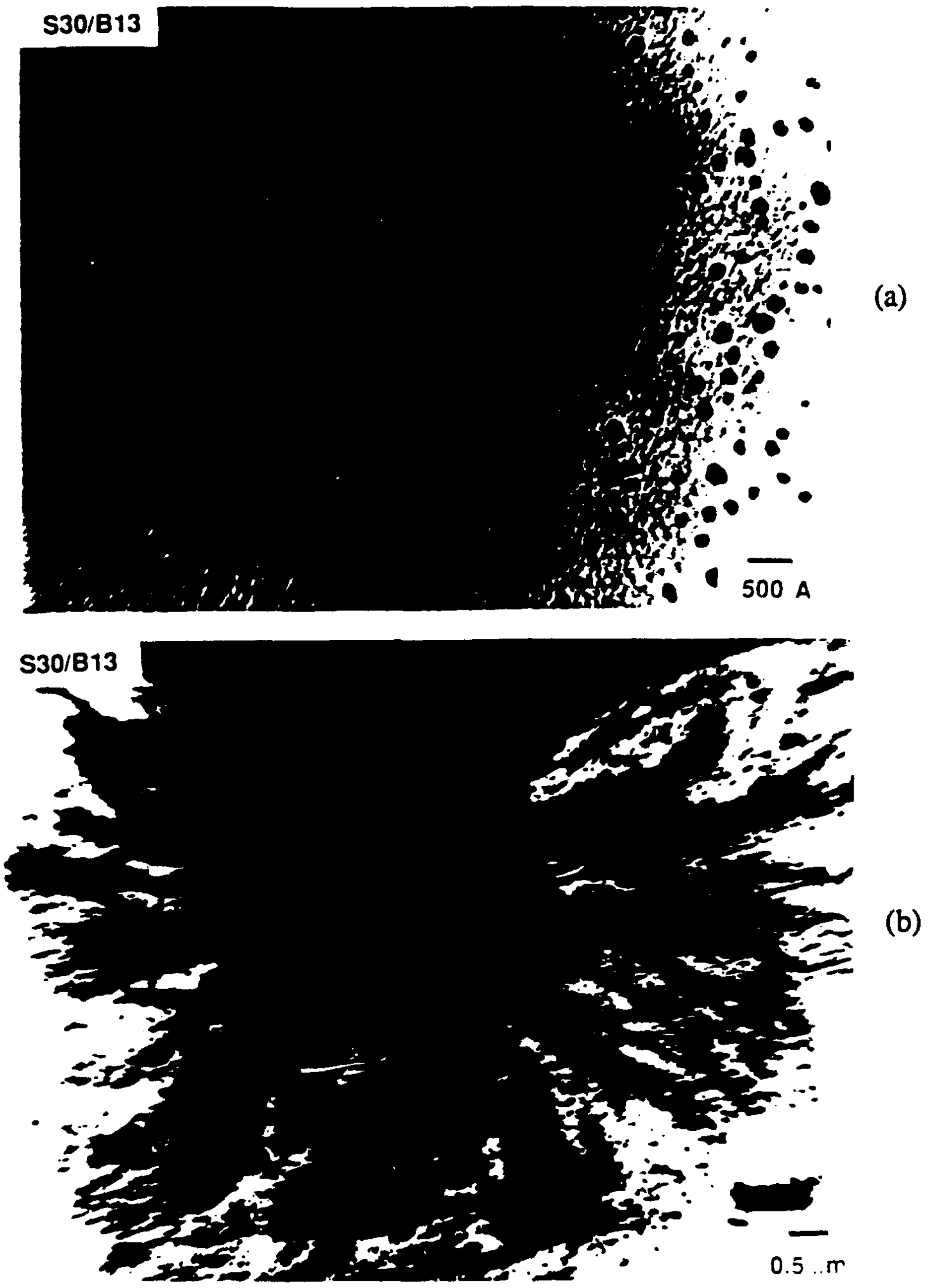


Figure 3.7 TEM micrographs of S30/B13 molded at approximately 260°C and subsequently annealed at 175°C for several hours. The uppermost micrograph (a) shows the regularity and scale of the microphase separated spherical morphology, while the lower magnification of micrograph (b) shows evidence of the growth of crystalline spherulitic structures.

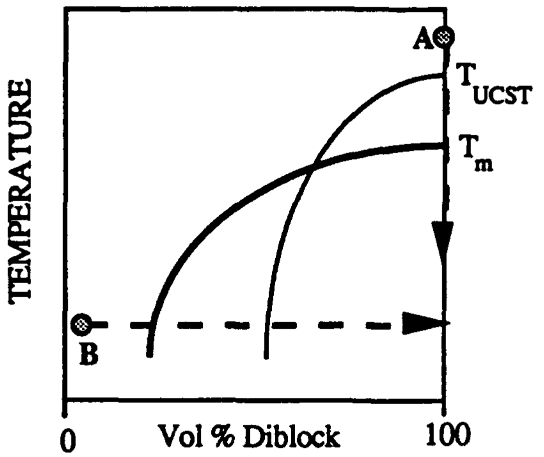


Figure 3.9 Simplified phase diagram for the S30/B13 semicrystalline diblock copolymer-solvent system

different final morphological picture. This once again reinforces the importance of clearly identifying not only the thermodynamic driving forces that lead to an equilibrium morphology but other external or kinetically driven processes as well.

IV EMULSIFICATION OF TERNARY BLENDS

4.1 Blends of Diblock Copolymers and Two Homopolymers

A considerable amount of experimental work has been conducted in the area of copolymer-homopolymer blends, and several theoretical treatments have been developed which attempt to describe the expected structure and mechanical behavior of such systems[1, 44-46]. These studies can be subdivided into two main categories. On the one hand, there is an interest in using copolymers as compatibilizers for incompatible blends, with total miscibility or at least partial miscibility on a microscale level as the primary goal. What is of greater relevance to this thesis is the work done on blends containing small quantities of block copolymers in blends with one or more of the corresponding homopolymers. The emphasis in this case is in the emulsifying potential of the block copolymers: by locating preferentially at the phase boundary[47], these materials can cause a finer domain dispersion and result in a decrease in the interfacial tension in the system, with diblock copolymers providing the most significant effect in this respect[48]. The degree of emulsification is a function of several factors. For example, a primary requirement is that the homopolymer molecular weights be smaller than the respective copolymer block segments in order for the emulsification effect to occur[49-51].

While most experimental evidence in the literature has focused on amourphous hydrocarbon systems, little information is available for the case where one or more of the homopolymers and block segments in the blend are semicrystalline. Experimental evidence has been collected in this lab for a limited number of semicrystalline systems[52-54]. What is generally observed is that the addition of small quantitites of the semicrystalline diblock material results in a significant change in the originally coarse morphology of the binary blend, with increasing diblock concentration corresponding to a reduction in the size of the dispersion. It is also clear, however, that the final structure depends strongly on a large number of parameters and cannot be as easily modeled in terms of a homogeneous matrix and a dispersed phase as in the analogous amourphous case. Processing techniques and crystallization temperatures for example have all been shown to contribute drastically in their effect on the final morphological picture of the system and need to be addressed when formulating a plan for the engineering of an effective semicrystalline blend.

4.2 Characterization of Emulsification Effect

Extensive characterization was conducted on the ternary blends by transmission electron microscopy, which provided information regarding the microscale morphology of the materials, and scanning electron microscopy, which focused on a more macroscale examination of the phase separation irregularities at a crack surface. The results of the emulsification analysis can be viewed in terms of the simplified diblock-iPS homopolymer-PB homopolymer ternary phase diagram shown in Fig.4.1. Starting with an examination of a basic binary blend, different incremental amounts of diblock were added to blends along the isopleth line of constant iPS-PB composition. At a critical diblock concentration, the system is expected to shift from a macrophase separated blend to the finer scale microstructure indicative of an emulsified system. This transition was found to be dependent on several factors such as diblock size and composition, processing method and, most importantly, the effect of crystallinity on the blend morphology. While in a block copolymer system crystallinity was seen to effectively engulf the existing phase separation without destroying it due to the connectivity of the diblock material, in an emulsified blend it could at times result in an aggregation or disruption

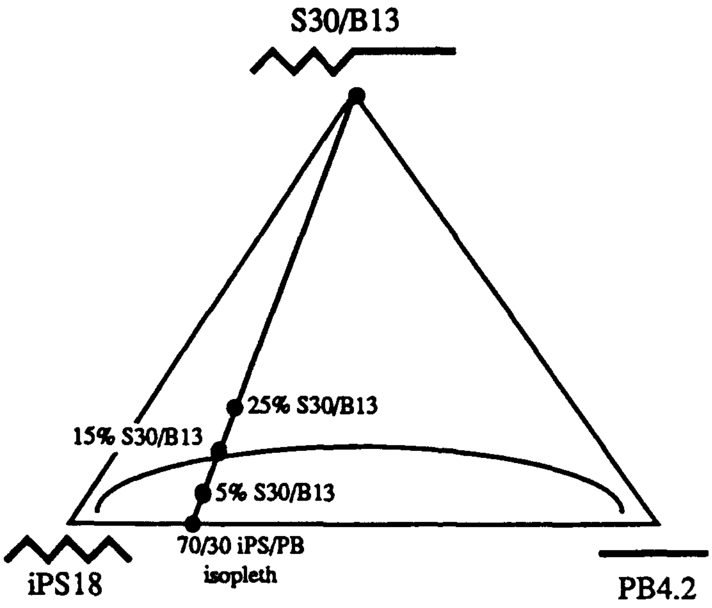


Figure 4.1 Schematic ternary phase diagram for 70/30 ternary blend system

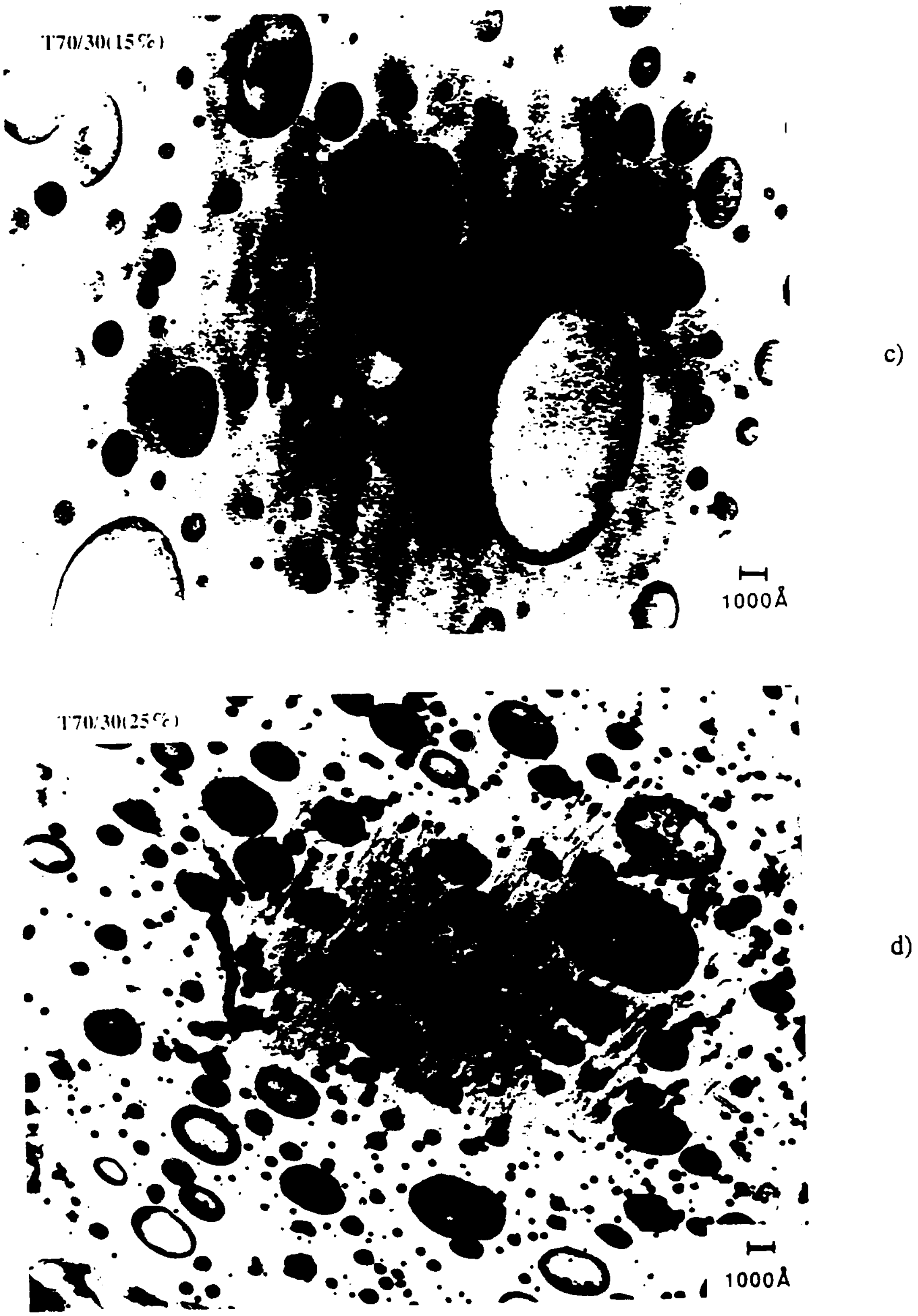
of the domain structure depending on the degree of interfacial tension provided by the copolymer. Two different sets of iPS-PB blends were examined. This section will focus on the binary blend of iPS18 and PB4.2 prepared in a 70/30 iPS to PB ratio which then served as a basis for subsequent ternary blending with the S30/B13 copolymer in samples of 0%, 5%, 15% and 25% diblock content.

The lack of any interfacial adhesion for the H70/30 binary homopolymer blend resulted in a stripping of the PB domains in the ultramicrotomed TEM films as evidenced by the "swiss cheese" phase separated structure observed in Fig.4.2a. The addition of only 5% diblock copolymer in the T70/30(5%) sample alleviated this problem to some extent, but a considerable variation in domain sizes and large scale sample defects still persisted throughout the material (Fig.4.2b). A major step change in the morphology is seen for sample T70/30(15%) with a 15% diblock content (Fig.4.2c). Microphase separation is now on the scale of hundreds of angstroms rather than microns, with a decrease in the number of larger domains and an observed improvement in the degree of adhesion between the phases as evidenced by the lack of any PB domain stripping. The emulsification effect is even more apparent in the T70/30(25%) TEM micrograph of Fig.4.2d as the diblock content is increased to 25%, where the regularity and scale of the dispersion begin to resemble those obtained for pure diblock copolymer. From these basic observations, an emulsification transition curve for the ternary diagram of Fig.4.1 is estimated to lie in the range of 10-20% diblock content for the case of the quenched amorphous isotactic polystyrene-polybutadiene ternary blend system.

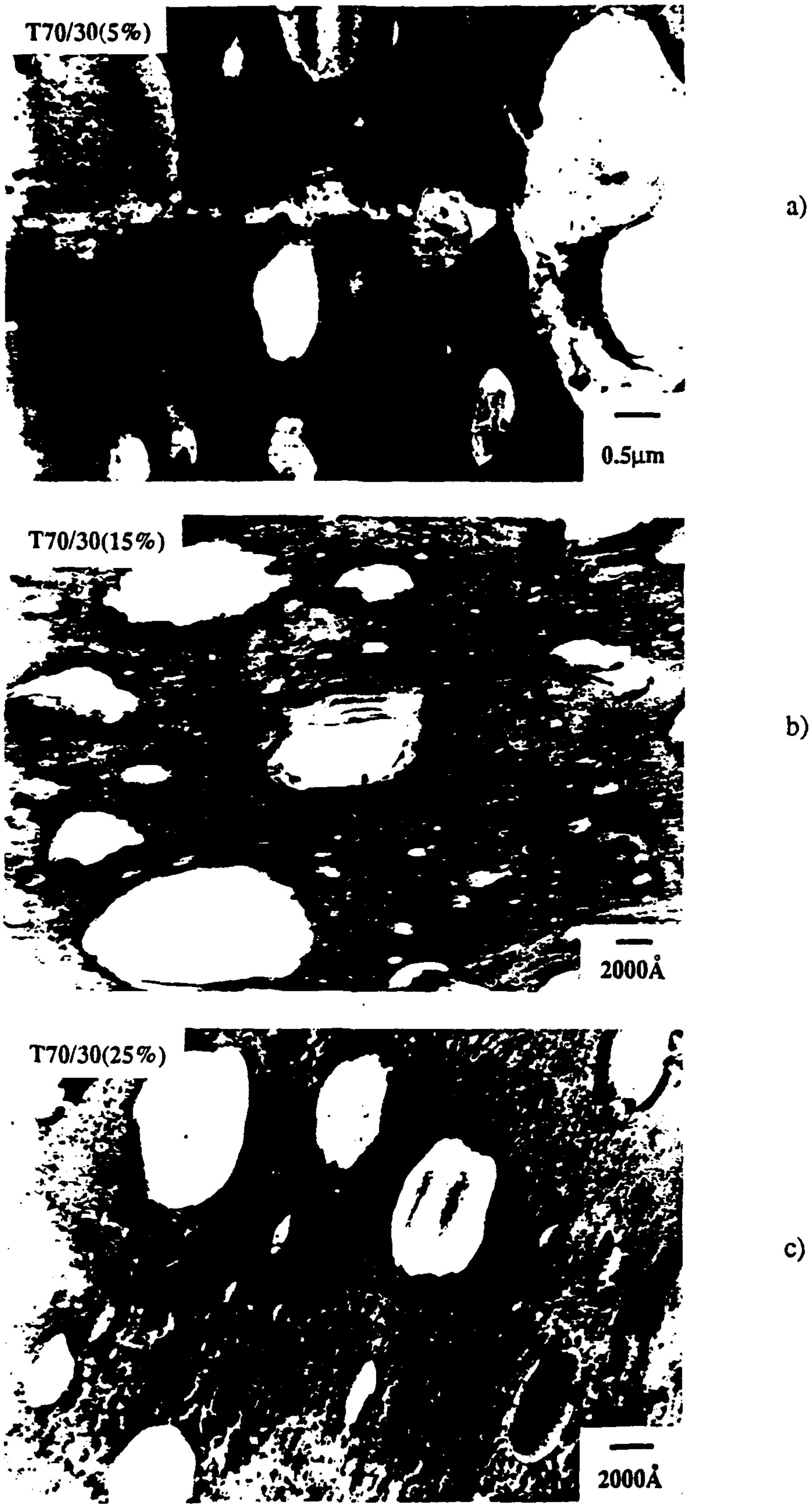
When the same four samples are annealed at 175°C for several hours, the effect of crystallinity is found to be strongly dependent on the amount of diblock present in the system. The binary blend proved to be too brittle and could not be effectively ultramicrotomed for TEM analysis. The crystallized T70/30(5%) sample of Fig.4.3a shows a considerable amount of domain aggregation and sample fracture which indicates poor interfacial adhesion between the phase separated domains. While there is evidence of some improvement in the morphology of the crystallized T70/30(15%) material (Fig.4.3b), only in the T70/30(25%) blend does the onset of crystallinity not destroy or cause any significant disruption of the original microstructure (Fig.4.3c). Though there is some PB domain aggregation, the regularity and scale of the phase separation is consistent with that observed for the amorphous case of Fig.4.2d. Furthermore, the vapor phase RuO_4 staining clearly highlights the crystalline lamellae structures that permeate the entire interdomain isotactic polystyrene matrix. These results indicate that a larger amount of S30/B13 diblock copolymer than noted for the amorphous case was required in the crystallized sample in order to provide enough interfacial adhesion between phase separated domains to maintain the original morphology in the presence of the imposed crystalline texture. The emulsification transition curve for these semicrystalline blends is estimated therefore to lie in the range of 20-30% diblock content in the ternary phase diagram of Fig.4.1.

The information obtained from the SEM analysis supports the general trends and observations discussed above, though on the larger scale of crack surfaces. Figs.4.4a-d show how the addition of diblock copolymer in amorphous samples results in a definite emulsification of the original coarse H92/8 binary blend morphology to a finer dispersion of PB domains in the 25% diblock content sample. The same trend is observed for the crystallized materials of Figs.4.5a-d. As in the TEM analysis, there appears to be more domain disruption and aggregation in the T70/30(15%) sample than observed for the amorphous case, indicating the need for a higher diblock concentration for a crystallized system.

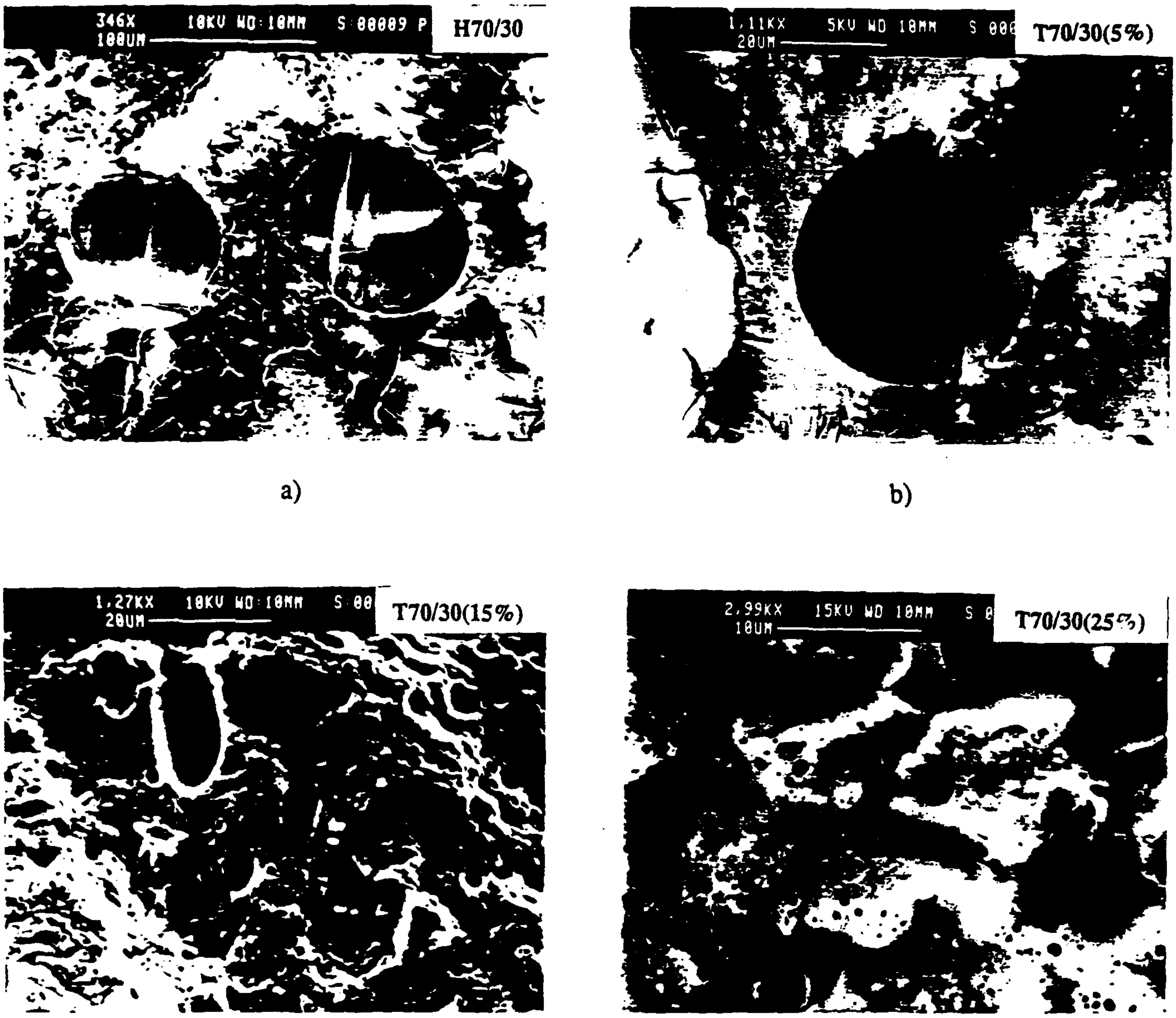
Figures 4.2a+b TEM analysis of amorphous 70/30 ternary blends of iPS18 and PB4.2 homopolymers with a) 0%, b) 5% S30/B13 diblock content prior to imposed crystallization



Figures 4.2c+d TEM analysis of amorphous 70/30 ternary blends of iPS18 and PB4.2 homopolymers with c) 15%, d) 25% S30/B13 diblock content prior to imposed crystallization



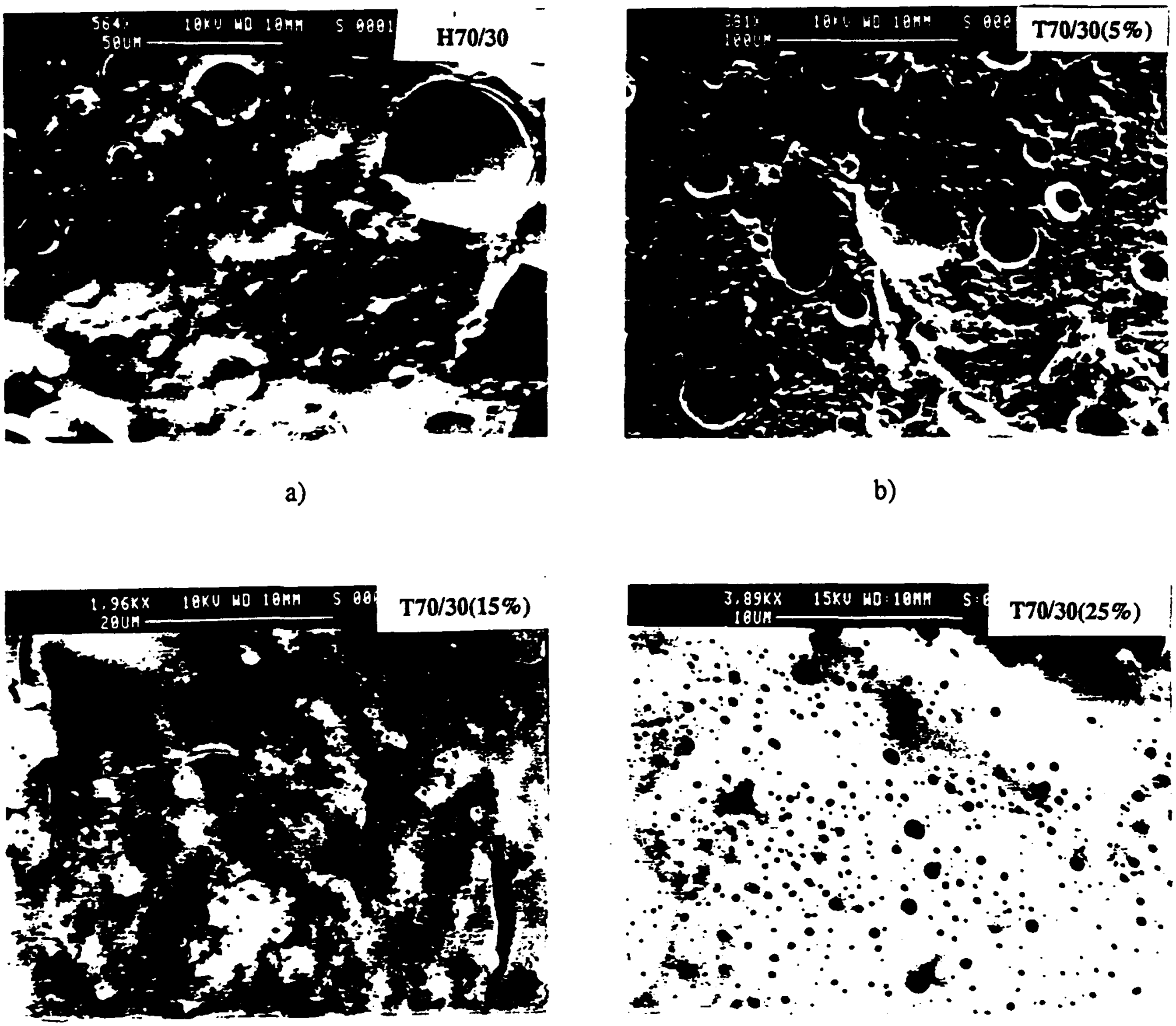
Figures 4.3 TEM analysis of 70/30 ternary blends of iPS18 and PB4.2 homopolymers with a) 5% b) 15% and c)25% S30/B13 diblock content after annealing at optimum crystallization temperature of 175°C for several hours



a) b)

c) d)

Figures 4.4 SEM analysis of amorphous 70/30 ternary blends of iPS18 and PB4.2 homopolymers with a) 0%, b) 5%, c)15% and d)25% S30/B13 diblock content prior to imposed crystallization



a)

b)

c)

d)

Figures 4.5 SEM analysis of 70/30 ternary blends of iPS18 and PB4.2 homopolymers with a) 0%, b) 5%, c)15% and d)25% S30/B13 diblock content after annealing at optimum crystallization temperature of 175°C for several hours.

V ANALYSIS OF MATERIAL TOUGHNESS

5.1 Fracture Mechanics Analysis

While a complete study of the rubber toughening of brittle polymers would involve a number of considerations such as particle distribution, domain sizes, the presence of dilbock copolymers at the interface, crystallinity and the effect of various mechanical deformation processes, the inherent toughness of a material can be easily determined by a simple analysis of its stress-strain behavior as generated by conventional tensile testing methods (i.e. Instron). The limited amount of material recovered from the low conversion iPS polymerizations was deemed insufficient for a proper analysis to be conducted with these techniques, which then prompted the search for alternate testing methods.

The study of fracture mechanics is based on the premise that the strength of a material is governed in large part by the presence of critical defects or flaws that result in cracks and general mechanical failure. A mathematical analysis of the propagation of cracks under stress can then serve to express the relative toughness of a sample in terms of parameters characteristic of such growth. One such parameter is the stress intensity factor K, which relates the magnitude of the stress-intensity local to the crack front in a linear elastic material in terms of the applied load and the geometry of the system[55]. For the case of a tensile crack loading geometry (Mode I), the stress intensity factor can be simply expressed as $K_I = Q \sigma a^{1/2}$[55], where 'a' is the crack length, σ is the applied stress at the onset of crack growth and Q is a parameter defined by the geometry of the system. When K_I reaches a critical value defined as K_{Ic}, crack propagation occurs. While K_I is a stress field parameter that is independent of the material, K_{Ic} is defined as a material property directly related to the toughness of the sample. A basic analysis of crack length vs. imposed stress was then opted for in the study of the emulsified blend system.

5.2 Micromechanical Toughness Analyzer

Fracture toughness for the emulsified blend samples was analyzed for the case of two symmetrical cracks emanating equatorially from a hole opened by an internal pressure p as shown in the following sketch:

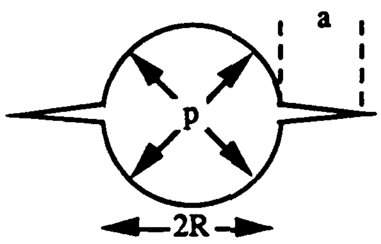


Figure 5.1

For this geometry the stress intensity factor is expressed as $K_I = p\sqrt{(\pi a)}\ F(s)$, where F(s) is a form factor based on the crack length 'a' and the hole radius R[56]. A special micromechanical toughness analyzer device was built for the purpose of this analysis and consisted simply of a micrometer driven wedge opening up two halves of a 1 mm wire placed through the hole, thus providing a displacement Δd which was visually monitored through a ligh microscope set-up. The internal pressure p can be expressed as a function of this displacement through the expression $\Delta d = 2p(1-\nu)a/\mu$[57], where ν and μ are the Poisson ratio and shear modulus respectively of the material as approximated from composite theory[58]. The stress intensity factor for this system can then be represented as:

$$K_I = \frac{\mu \Delta d F(s)}{2(1-\nu)}\sqrt{\frac{\pi}{a}} \tag{5.1}$$

where:

$$F(s)=1+\left(\frac{a}{R+a}\right)\left(0.5+0.743\left(1-\frac{a}{R+a}\right)^2\right) \tag{5.2}$$

The S100/B52 diblock copolymer was blended with iPS57 and PB25 homopolymers to provide three different samples of 92/8 iPS-PB composition with 0%, 7%, and 14% diblock content.

5.3 Results of Fracture Toughness Analysis

A qualitative understanding of the relative strength of the crystallized blends was obtained through a simple plot of the opening displacement Δd versus the propagating crack length 'a' as shown in Fig.5.2. The data for High Impact Polystyrene (HIPS) and atactic polystyrene homopolymer (aPS) are presented as examples of the two extremes of very tough and very brittle materials respectively. As expected, the diblock copolymer parallels the behavior of the tough HIPS, while the lack of any interfacial adhesion in the semicrystalline homopolymer blend results in a brittle material comparable to the glassy atactic polystyrene. The addition of only 7% diblock does not appear to have a beneficial

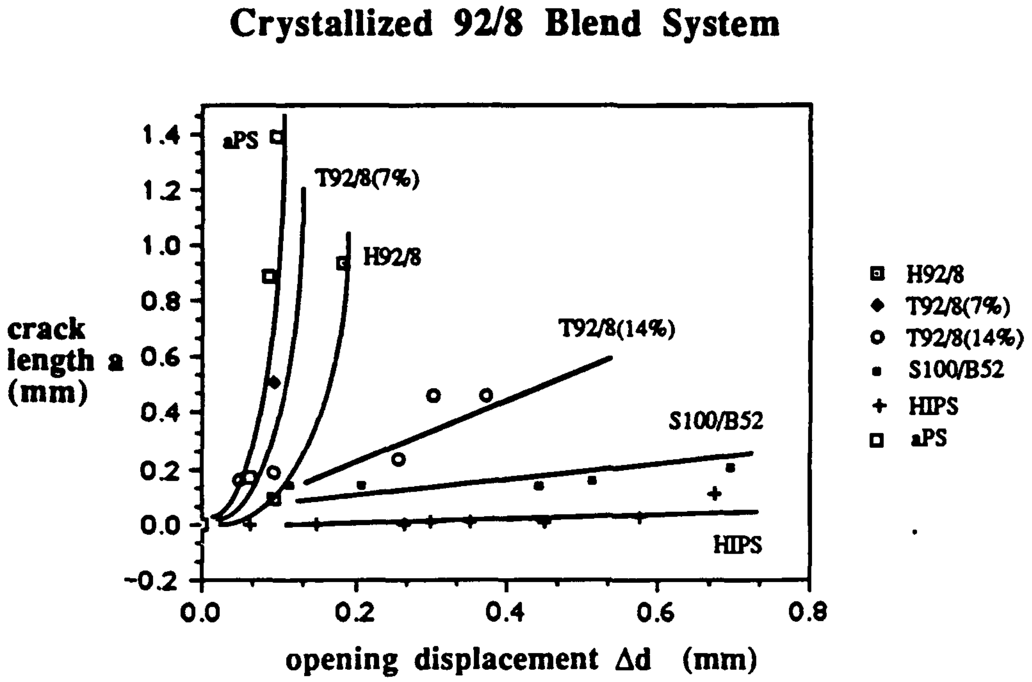


Figure 5.2 MTA device results: plot of opening displacement vs. crack length

effect on the blended system, as the sample displays the same behavior as the binary blend. The *T92/8(14%) sample however shows a significant* improvement in toughness as indicated by a lower slope in the data. This effect is attributed to the presence of a sufficient amount of diblock copolymer to achieve an emulsified morphology with a higher level of interfacial adhesion than the 7% diblock content blend.

While this plot serves to qualitatively describe the interfacial properties of the examined materials, more quantitative values of K_I could not be accurately determined. The original definition of the stress intensity factor is based on the concept of linear elastic fracture mechanics for materials which obey Hooke's law, where stress is proportional to infinitesimal strains. Deviations in this linear behaviour away from the crack tip, the introduction of crazing phenomena preceeding fracture and sample thickness variations for example lead to significant deviations in the value of K_{Ic}. While accurate numbers were unattainable, trends were however observed that paralleled those presented in Fig. 5.2, with K values rising for increasing amounts of added diblock copolymer.

VI CONCLUSIONS

The engineering of novel polymeric materials through the physical blending of preexisting polymers involves a sophisticated mix of chemistry and processing knowhow that essentially translates into a control over the final microstructure of the material. The emulsification of incompatible blends through the use of diblock copolymers presents one alternative in achieving this level of control by establishing a trade-off between the inexpensive but ineffective binary blend of homopolymers and the more complex but structurally more desirable block copolymers.

This work has addressed the problem of emulsification in isotactic polystyrene-polybutadiene blends from the initial step of material preparation up to preliminary mechanical testing evaluations. A novel low temperature anionic synthesis technique was successfully developed for the preparation of the iPS[11] and was considered a significant contribution to the literature in the area of diblock copolymer anionic polymerization due to its applicability to subsequent copolymerization schemes. Semicrystalline diblocks of iPS and PB were successfully prepared by sequential polymerization or homopolymer coupling and were thoroughly characterized to establish unequivocally the diblock nature of the receovered product. A morphology analysis of the diblock material reaffirmed the need for characterizing the level of interaction between the thermodynamics of phase separation and the kinetically driven crystallization phenomena when dealing with such materials. The onset of crystallization did not appear to disrupt or destroy an existing phase separated morphology but rather incorporated it into the crystalline texture. When it occurs in a homogeneous melt, however, it effectively supresses ordered microphase separation and results in an exclusion of the rubber from the growing crystalline front.

Finally, the results of the emulsification study proved the effectiveness of the semicrystalline diblocks in providing finer dispersion and increased interfacial adhesion in the incompatible homopolymer blend. This effect was clearly demonstrated through a visual examination of the microscale morphology and further substantiated by the results of a preliminary mechanical testing study. The use of fracture mechanics theory in the analysis of the emulsified blends presents an interesting approach to the study of material toughness that however needs to be developed more fully in terms of device design, sample preparation and data acquisition.

VII REFERENCES

1. Paul, D.R. In *Polymer Blends* ; Paul, D.R.; Newman, S., Eds.; Academic Press: New York, 1978.
2. Krause, S. In *Polymer Blends* ; Paul, D.R.; Newman, S., Eds.; Academic Press: New York, 1978.
3. Rakestraw, J.K. Ph.D. Thesis, Massachusetts Institute of Technology, 1990.
4. Szwarc, M. *Nature* **1956**, *178*, 1168.
5. Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656.
6. Boor, J. *Ziegler-Natta Catalysts and Polymerizations* ; Academic Press: New York, 1979.
7. Kern, R.J. *Nature* **1960**, *187*, 410.
8. Kern, R.J. U.S. Patent 3 459 882,1960.
9. Braun, D.; Betz, W.; Kern, W. *Makromol. Chem.* **1960**, *42*, 89.
10. Worsfold, D.J.; Bywater, S. *Makromol. Chem.* **1963**, *65*, 245.
11 Cazzaniga, L.A.; Cohen, R.E. *Macromolecules* **1989**, *22*, 4125.
12. Gnanou, Y.; Rempp, P. *Makromol. Chem.* **1987**, *188*, 2111.
13. Quirk, R.P.; Chen, W. *Makromol. Chem.* **1982**, *183*, 2071.
14. Hirao, A.; Hattori, I.; Sasagawa, T.; Yamaguchi, K.; Nakahama, S. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 59.
15. Schulz, D.N.; Halasa, A.F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2401.
16. Kawamura, T.; Uryu, T.; Matsuzaki, K. *Makromol. Chem.* **1979**, *180*, 2001.
17. Granger, A.T.; Wang, B.; Krause, S.; Fetters, L.J. In *Multicomponent Polymer Materials* ; Paul, D.R.; Sperling, L.H., Eds.; American Chemical Society: Washington, D.C., 1986;
18. Meier, D.J. *J. Polymer Sci.: Part C* **1969**, 81.
19. Meier, D.J. *ACS Polymer Preprints* **1970**, *11*, 400.
20. Helfand, E.; Wasserman, Z.R. *Polym. Eng. Sci.* **1977**, *17*, 582.
21. Helfand, E.; Wasserman, Z.R. In *Developments in Block Copolymers* ; Goodman, I., Eds.; Applied Science Publishers: New York, 1982; pp 99.
22. Hong, K.M.; Noolandi, J. *Macromolecules* **1981**, *14*, 727.
23. Hong, K.M.; Noolandi, J. *Macromolecules* **1981**, *14*, 736.
24. Hong, K.M.; Noolandi, J. *Macromolecules* **1983**, *16*, 1083.

25. Noolandi, J.; Hong, K.M. *Macromolecules* **1982**, *15*, 482.

26. Meier, D.J. In *Polymer Blends and Mixtures* ; Walsh, D.J.; Higgins, J.S.; Macconnachie, A., Eds.; Martinus Nijhoff Publishers: Boston, 1985; pp 173.

27. Leibler, L. *Macromolecules* **1980**, *13*, 1602.

28. Cohen, R.E. In *Elastomers and Rubber Elasticity* ; 1982;

29. Cohen, R.E.; Wilfong, D.E. *Macromolecules* **1982**, *15*, 370.

30. Aggarwal, S.L. *Polymer* **1976**, *17*, 938.

31. Alward, D.B.; Kinning, D.J.; Thomas, E.L.; Fetters, L.J. *Macromolecules* **1986**, *19*, 215.

32. Kinning, D.J.; Alward, D.B.; Thomas, E.L.; Fetters, L.J.; Handlin, D.J. *Macromolecules* **1986**, *19*, 1288.

33. Thomas, E.L.; Alward, D.B.; Kinning, D.J.; Handlin, D.L.; Fetters, L.J. *Macromolecules* **1986**, *19*,

34. Herman, D.S.; Kinning, D.J.; Thomas, E.L.; Fetters, L.J. *Macromolecules* **1987**, *20*, 2940.

35. Hasegawa, H.; Tanaka, H.; Yamasaki, K.; Hashimoto, T. *Macromolecules* **1987**, *20*, 1651.

36. DiMarzio, E.A.; Guttman, C.M.; Hoffman, J.D. *Macromolecules* **1980**, *13*, 1194.

37. Whitmore, M.D.; Noolandi, J. *Macromolecules* **1988**, *21*, 1482.

38. Lotz, B.; Kovacs, A.J.; Bassett, G.A.; Keller, A. *Koll. Zeit. fur Zeit. Poly.* **1966**, *209*, 115.

39. Gervais, M.; Gallot, Y. *Makromol. Chem.* **1973**, *171*, 157.

40. Seow, P.K.; Gallot, Y.; Skoulios, A. *Makromol. Chem.* **1976**, *174*, 193.

41. Hay, J.N.; McCabe, J.F. *J. Poly. Sci. (Chem.)* **1978**, *16*, 2893.

42. Hay, J.N.; Wiles, M. *J. Poly. Sci. (Chem.)* **1979**, *17*, 2223.

43. Hirata, E.; Ijitsu, T.; Soen, T.; Hashimoto, T.; Kawai, H. *Polymer* **1975**, *16*, 249.

44. Schmitt, B.J. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 273.

45. Bywater, S. *Polym. Eng. Sci.* **1984**, *24*, 104.

46. Roe, R.-J.; Rigby, D. *Adv. Polym. Sci.* **1987**, *82*, 103.

47. Noolandi, J.; Hong, K.M. *Macromolecules* **1984**, *17*, 1531.

48. Riess, G.; Jolivet, Y. In *Copolymers, Polyblends, and Composites* ; Platzer, N.A.J., Eds.; Amer. Chem. Soc.: Washington, D.C., 1975; pp 243.

49. Kawai, H.; Hashimoto, K.; Miyoshi, K.; Uno, H.; Fujimura, M. *J. Macromol. Sci., Phys. B* **1980**, *17*, 427.

50. Hashimoto, H.; Fujimura, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1981**, *14*, 844.

51. Riess, v.G.; Kohler, J.; Tournut, C.; Bandaret, A. *Makromol. Chem.* **1967**, *101*, 58.

52. Drzewinski, M.A. Ph.D. Thesis, Massachusetts Institute of Technology, 1986.

53. Veith, C.A. Ph.D. Thesis, Massachusetts Institute of Technology, 1989.

54. Del Giudice, L.; Cohen, R.E.; Attalla, G.; Bertinotti, F. *J. Appl. Poly. Sci.* **1985**, *30*, 4305.

55. Irwin, G.R. *Appl. Mats. Res.* **1964**, *3*, 65.

56. Tada, H.; Paris, P.C.; Irwin, G.R. *The Stress Analysis of Cracks Handbook* ; Del Research Corporation: Hellertown, USA, **1973**.

57. Green, A.E.; Zerna, W. *Theoretical Elasticity* ; Clarendon Press: Oxford, **1954**

58. Argon, A.S.; Cohen, R.E.; Gebizlioglu, O.S.; Schwier, C.E. ; Kausch, H.H., Eds.; 1983; pp 275.