TACTICITY IN VINYL POLYMERS

Introduction

Tacticity in polymers refers to a configurational order in molecular structures. Definition of polymer tacticity is properly given in a review article by Jenkins and co-workers (1), which reads

> The orderliness of the succession of configurational repeating units in the main chain of a regular macromolecule, a regular oligomer molecule, a regular block or a regular chain.

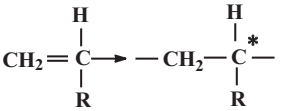
Tacticity should not be confused with the conformational states of the polymer chains in space. The conformation refers to different arrangements of atoms and/or substituents of the polymer chain brought about by rotations about single bonds. Examples of different polymer conformations include the fully extended planar zig-zag, helical, folded chains, and random coils, etc. By contrast, the tactic configuration of the molecular chains refers to the organization of the atoms along the chain and configurational tactic isomerism involves the different structural arrangements of the atoms and substituents in a polymer chain, which can be interconverted only by the breakage and reformation of primary chemical bonds. There are three tactic forms in polymers: atactic, isotactic, and syndiotactic. Isotactic and syndiotactic polymers are both stereoregular and thus are crystallizable. Atactic polymers, on the other hand, are usually completely amorphous, unless the side group is so small or highly polar as to permit crystallinity, e.g. poly(vinyl fluoride) (PVF) or polyacrylonitrile (PAN). Like some organic compounds or naturally occurring polymers such as poly(L,D-lactic acid)s or poly(amino acid)s that differ in chirality, vinyl polymers differ in tacticity, which may be viewed as a pseudochirality form.

Tacticity in polymers is part of stereochemistry of organic materials. For references, readers are advised to refer to the comprehensive definitions and notations related to tacticity and other stereochemistry of polymers or organic compounds expertly addressed in a comprehensive review article (2), which later was adapted by IUPAC Recommendations 1980 in *Compendium of Macromolecular Terminology and Nomenclature*, 2nd edition, Chapter 2, "Stereochemical Definitions and Notations Relating to Polymers." Differences in either tacticity or other types of stereoregularity in natural polymers are also common. Such concepts are widely used by nature to produce a variety of compounds of different properties or functions from same chemical species. Examples of different geometric

stereoregularity are seen in natural rubbers versus gutta percha, cellulose versus starch, etc, and differences of molecular stereoregularity in these natural polymers can result in significantly different mechanical and physical properties. In general, unlike difference in chirality that causes only optical properties but little differences in other physical properties in molecules or polymers, by contrast, differences in tactic or geometric stereoregularity in synthetic polymers or natural polymers result in significantly different properties. Tacticity in polymers causes phenomenal differences in microstructures, morphology, crystalline polymorphism, and physical/mechanical properties. Generally, tacticity in polymers is not 100%. A percentage of a specific tacticity can usually be characterized by using high-resolution solid-state nuclear magnetic resonance. Isotacticity in three consecutive monomer sequence is the placement called a meso-(same side) or m-placement; the syndiotactic structure corresponds to a racemic-(opposite) or r-placement. Each of these tactic combinations can be distinguished through NMR techniques.

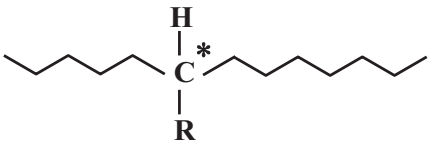
Definition of Tacticity in Polymers

Tacticity in polymers is one type of stereoregular forms in molecular configurational structures. Polymers with specific tactic configurations can be viewed as pseudochiral polymers. The tactic polymers are, however, not really chiral and do not have chirality at all. Tacticity configuration is seen in vinyl polymers with mono- or disubstituted groups. The polymerization of monosubstituted ethylene, such as a vinyl compound, leads to polymers in which every other carbon atom is a potential chiral center. This center is marked with an asterisk, as follows (3):



(1)

Such carbon atoms are referred to as pseudochiral centers in long-chain polymers because the polymers do not in fact exhibit optical activity (4). The reason for the lack of optical activity in tactic polymers can be seen through a closer examination of the substituents on such pseudochiral center:



(2)

The two chain segments to left and right sides of the center carbon are in general of unequal segmental length, and thus they are structurally different "groups." However, in reality, only the first few atoms of the two chain segments attached to C* are responsible for the optical activity, not those farther away. These neighboring atoms to C* are seen to be the same, and hence the polymer is

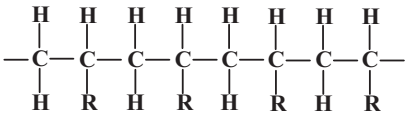
optically inactive (unable to cause optical rotation), even though the segments to the right and left-hand sides of C* are different. More comprehensive definition of a term related to "pseudoasymmetric" defined for the carbon atom is referred to the Farina's historical review book chapter (5). This term and definition, however, is out of the scope of this chapter.

Spatial Three-Dimensional View of Tacticity. Using Fischer–Hirshfelder or similar models, the actual differences between isotactic and syndiotactic vinyl-type polymers can be illustrated (see the equation below) as

(3)

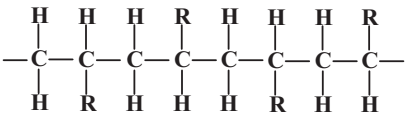
where the dangling bonds on two ends refer to continuing main backbone. In the three-dimensional (3-D) schemes, the medium-size blue ball indicates a substituent group and the others are carbon and hydrogen atoms. For isotactic polymers, the substituent groups are all on the same side of carbon all-trans zigzag plane; for syndiotacticity, the substituent groups are alternatively on the opposite side of the carbon all-trans zigzag plane.

A two-dimensional (2-D) analogue can be made using Fisher projections. In these 2-D projections, the R groups are placed either up or down. All up- (or all down-) positions of R indicate the isotactic structure:



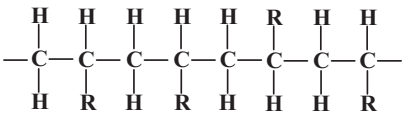
(4)

Alternating up –and down positions indicate the syndiotactic configuration



(5)

And random up and down positions indicate the atactic configuration



(6)

In specifying the tacticity of the polymer, the prefixes it- (or i-) and st- (or s-) are placed before the name or structure to indicate isotactic and syndiotactic structures, respectively. For example, it-polystyrene (or i-PS) means that the

polystyrene is isotactic. The term i-PVC [poly(vinyl chloride)] means isotactic-PVC, and so on. Such tactic polymers are known as stereoregular polymers. The absence of these tactic terms in polymer names denotes the corresponding atactic structures; for example, PS or poly(methyl methacrylate; PMMA) means atactic PS or atactic PMMA, respectively, and they are usually noncrystalline and amorphous owing to the lack of an stereoregularity order. Tacticity usually is seen in monosubstituted vinyl polymers, although in principle 1,2-disubstitued polymers may also display four different forms of ditactic regularity. Ditactic 1,2-disubstituted polymers, however, are not as common as monotactic polymers (tactic vinyl polymers with a single substituent). Tritacticity in polymers is also possible when the monomer units contain two tactic sites plus an additional double bond, for example, resulting in a total of three tactic sites. Several examples of ditactic and tritactic polymers can also be seen in IUPAC Recommendations 1980 in *Compendium of Macromolecular Terminology and Nomenclature*, 2nd edition, Chapter 2 "Stereochemical Definitions and Notations Relating to Polymers" (2).

Tacticity and Properties of Polymers. The structures as shown in the schemes for different tactic configurations may result in profoundly different physical and mechanical properties in polymers. The isotactic and syndiotactic structures are both crystallizable because of their regularity along the chain. However, their unit cells and melting temperatures are not the same. Atactic polymers, on the other hand, are usually completely amorphous, unless the side group is so small or the polymers are so polar as to permit some crystallinity, for example, in PVF. Tacticity in molecular structures influenced the glass transition and melting points. Syndiotactic polymers usually have a higher T_g than the isotactic forms of the same polymer. For example, isotactic PMMA (i-PMMA; weight-average molecular weight $M_w = 300{,}000$) has a $T_g = 52^\circ$C, but syndiotactic PMMA (s-PMMA; $M_w = 50{,}000$) has a much higher $T_g = 124^\circ$C. Polymer chains are obviously more flexible, thus have a lower T_g, when the pendant group is all aligned on the same side (isotacticity). Syndiotactity in polymers leads to higher T_g than isotacticity. Atactic PMMA (a-PMMA) has a T_g in between these two tactic forms, with $T_g = \sim 100^\circ$C.

Experimental Techniques and Apparatus for Tactic Polymers Characterization

Instrument for characterizing tactic polymers covers a variety of spectroscopic, thermal analysis, and microscopic techniques. Some of most commonly used are briefly listed here. Differential scanning calorimetry (DSC) is widely used for characterizing thermal properties, glass transition, crystallization kinetics, crystal polymorphism, and melting/crystallization transitions of tactic polymers. Wide-angle x-ray diffraction is widely used for determination of crystallinity and polymorphism, and crystal cell analysis on tactic polymers samples, with copper K_α radiation and a wavelength of 0.1524 nm. The scanning 2θ angle typically ranges from 5° to 40° with a step speed of 2° min^{-1}.

Microscopic characterization is utilized for analyzing the polymorphism, lamellar or spherulitic morphology of interior and surface of polymers. Polarized-light optical microscopy (POM), usually equipped with a CCD (charge-coupled

device) digital camera and a microscopic hot stage, is very useful for characterizing the phase domains or crystalline morphology, especially spherulites or dendrites, of tactic polymers. Growth kinetics and rates analyses of spherulites can also be measured by using automated software of image processing for POM. Transmission electron microscopy (TEM) or scanning electron microscopy (SEM) is used to characterize the crystalline lamellar morphology of tactic polymers. For TEM, microtoming of samples into ultrathin films using a diamond knife is required. Sometimes, samples may also be prepared as ultrathin films by solvent casting and are carefully picked up by using a copper grid. For SEM, the surfaces (deposited on glass slide or silicon) must be coated with vapor-deposited gold using vacuum sputtering prior to SEM characterization. Atomic-force microscopy (AFM) is a relatively newer microscopic characterization technique. An intermittent tapping mode is more common for obtaining the AFM phase and height images. For polymers as soft matters, the scan range of the AFM scanner is better to cover as much as 150 μm $\times$ 150 μm, with a narrower area of 5 μm $\times$ 5 μm for selective focusing into spots of interest. The modern-day AFM software is capable of tracking along a marked line for height profiling and a variety of useful analyses to compile images for surface crystal morphology or phase domains in tactic polymers.

Fourier-transform infrared spectroscopy (FT-IR) is used for investigating crystal forms, polymorphisms in tactic polymers. Spectra may be obtained at 4 cm^{-1} resolution, and averages of spectra are from at least 64 scans (for enhanced signals) in the standard wave number range 400–4000 cm^{-1}. Samples for IR measurements are cast as thin films with a uniform thickness directly on KBr pellets at ambient temperature, and IR measurements are performed on the samples cast on KBr pellets. For determining the tacticity and other configuration forms, solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR) or solution-state ^{1}H NMR techniques (also Fourier transformed) are powerful tools. Tetramethylsilane is used as an internal standard for chemical shift references. Quantitative analysis based on the chemical shifts related to specific configurations in the tactic polymers can be performed to reveal tacticity forms and tactic percentages in tactic polymers.

Tactic Poly(methyl methacrylate): a-PMMA, i-PMMA, and s-PMMA

Vinyl polymers, when synthesized using suitable catalysts, can be produced to assume a fixed configuration, called tacticity, which is one type of stereoregularity. PMMA, poly(vinyl chloride), polypropylene (PP), poly(1-butene), PS, and so on are some common examples showing different tacticities, or low tacticity. Polymers of no tacticity (ie, atactic polymers) are generally amorphous. Polymers of sufficient tacticity degrees are usually crystallizable, with the crystallinity depending on the degrees of tacticity.

In 1956, polymer of methyl methacrylate (MMA) was first synthesized using anionic polymerization by Szware and Rembaum (6). In 1958, stereoregular PMMA was prepared by Fox and co-workers (7). They reported that the stereoregular PMMA prepared with 9-fluorenyl lithium in 1,2-dimethoxyethane at –60°C was used as an initiator (7). In 1983, another type of living polymerization for

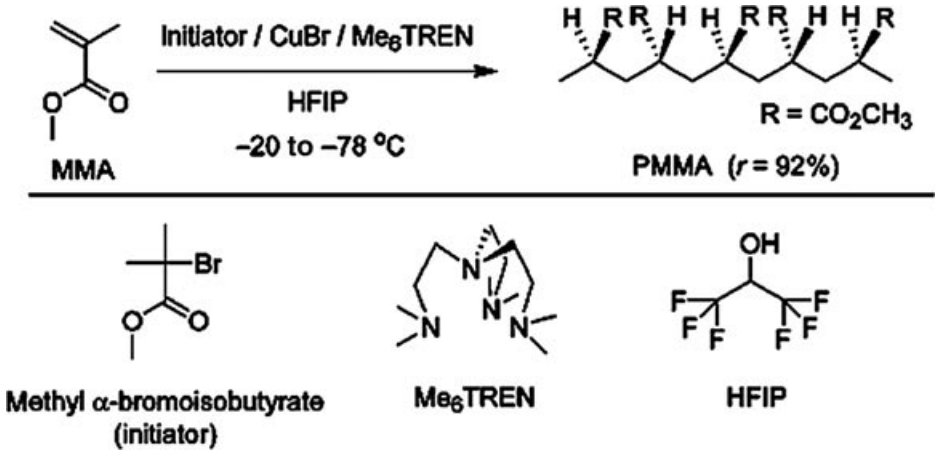


Fig. 1. Atom-transfer radical polymerization design for controlling the M_w and tacticity of PMMA. Reprinted from Ref. (12) with permission from the American Chemical Society. (Postnote: $r = 92\%$ in figure may be $rr = 92\%$.).

stereoregular PMMA, known as group transfer polymerization (GTP), was reported by Webster and co-workers (8). The narrow molecular weight distribution (MWD) of stereoregular PMMA can be produced by using the GTP method (9–11). More recently, the controlled/living radical polymerization was reported for controlling stereoregular polymers with targeted molecular weights and narrow MWD by Matyjaszewski and co-workers (12–14) and Kakuchi and co-workers (15). For example, Kakuchi and co-workers reported that the simultaneous control of the molecular weight and stereoregular PMMA was successfully accomplished by using the atom transfer radical polymerization with the methyl α-bromoisobutyrate/copper(I) bromide ($CuBr/Me_6TREM$) imitating system in HFIP at low temperature as shown in Figure 1. Stereoregulation in polymers and the idea of using F-alcohol is more comprehensively summarized in a review article (16). However, the specific control of tacticity by strongly polar F-alcohol may be interesting and novel, but some investigators questioned that such a phenomenon might be due to low temperature used in synthesis. These aspects are out of the scope of this chapter.

Tacticity and Crystalline Properties of PMMA

Since the first report on preparation of stereoregular PMMA by Szware and Fox (7), several articles reported that three types of isomeric forms were found in PMMA, such as i-PMMA, s-PMMA, and a-PMMA. A wide variety of properties of PMMA is displayed depending on degree of tacticity, such as glass transition temperature (T_g) (17–20), thermal degradation (T_d) (21), specific heat (C_p) and entropy (18), and viscoelastic properties (22). i-PMMA shows a T_g around 50°C and melting temperature (T_m) around 150°C depending on degree of tacticity, whereas s-PMMA shows a higher T_g around 120°C (17–20). Since a-PMMA is

mainly composed of syndiotactic units, the T_g of a-PMMA at around 100°C is much closer to the T_g of s-PMMA but far away from that of i-PMMA ($T_g = 50°C$) (17–20). Other properties, such as crystal structure (23–26), conformational energy (27,28), permeability properties (29), surface activity (30), and adsorption behavior (31), are also influenced by the type and degree of tacticity of PMMA. Several crystal structure models of i-PMMA have been proposed (23–26). Tadokoro and co-workers (25) reported that i-PMMA structure was formed by adopting a 10_1 double-stranded helix as a molecular model and crystallized in an orthorhombic lattice cell with the parameters $a = 41.96$ Å, $b = 24.34$ Å, and c (fiber axis) = 10.50 Å. By comparison, s-PMMA does not crystallize in melt crystallization at all, indicating poor crystallizability, but it may show a well-oriented crystalline structure by preparing in some specific organic solvents (26).

Effects of Tacticities on Phase Behavior of Blends

Over the past few decades, numerous reports on miscibility of polymers of different tacticities have been published. The miscibility of a polymer with another polymers of tactic forms has been reported to be different, such as blends of atactic PS with tactic poly(viny1 methyl ether; PVME) (32). It has been found that isotactic PVME (i-PVME) was less miscible with atactic PS (a-PS) than syndiotactic PVME (s-PVME) with a-PS (32). Blends of atactic PVME with tactic PS (a-PS and s-PS) have also been investigated. A study by Woo and Mandal (33) has concluded that the behavior of syndiotactic polystyrene (s-PS)/PVME blend agrees mostly with that of a-PS/PVME, indicating that tacticity or crystallinity in s-PS does not affect the phase behavior of s-PS/PVME in the amorphous domain. The phase behavior of a blend of PVME with s-PS tends to be quite similar to that of a blend of PVME with a-PS, indicating that tacticity in PS does not influence much the phase behavior in blends where the intermolecular interactions between two polymers are not based on configurational differences. The influence of tacticity on the phase behavior may be dependent on the interaction strength between two polymers, and effects of tacticity alone may be less influential when other factors are stronger.

Effects of Tacticity on the Phase Behavior in Blends with Different Tactic PMMA. The miscibility of a-PMMA with other polymers is often similar to that of blends of s-PMMA with the same polymers; however, the T_g–composition relationships may differ slightly. This is quite understandable because a-PMMA is mainly composed of a significant percentage of syndiotactic units in the main chains. Some blends with a-PMMA or s-PMMA are miscible based on the observation of composition-dependent glass transition temperature (T_g) in blends, but blends with i-PMMA are immiscible, such as poly(*N*-vinyl pyrrolidone) (34), poly(ethylene oxide) (PEO) (35), and poly(styrene-*co*-acrylonitrile) blends (36). Other factors, such as the mixing ratio (25), solvent effects (37,38), and molecular weight (39) of the polymer constituents, also influence the miscibility of tactic PMMA blends.

Owing to increasing importance of biodegradable polymers, blends of biodegradable polymers, such as poly(L-lactide) (PLLA) or poly(hydroxylbutyrate) (PHB) with PMMA have been widely studied. Biodegradable polyesters (PLLA

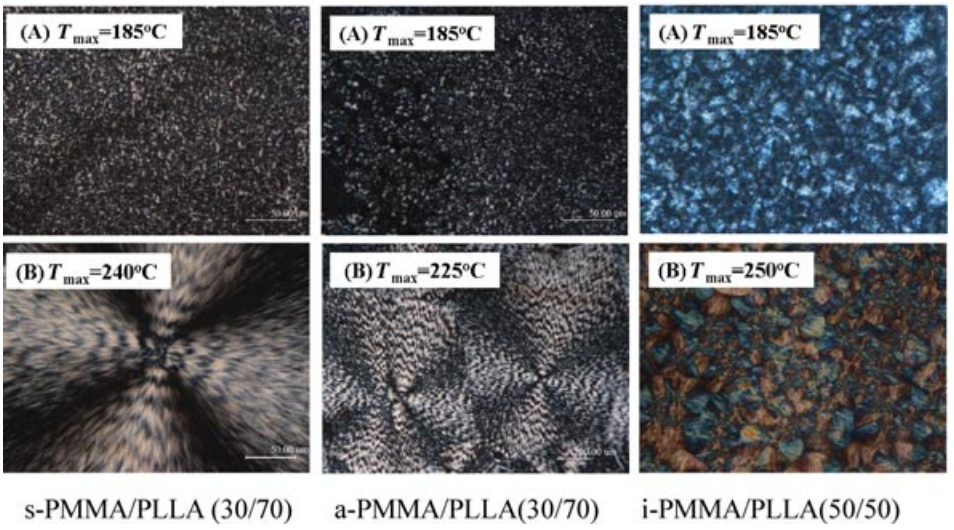


Fig. 2. POM graphs of PLLA spherulites in blends of various tacticities PMMA melt from the temperature below UCST (**A**) and above UCST (**B**). $T_c = 130°C$. Reprinted from Ref. (36) with permission from the John Wiley and Sons.

or PHB) are often modified with PMMA to improve their properties for service environments. However, the phase behavior and miscibility of biodegradable PLLA with tactic PMMAs can be ambiguous and remain to be quite controversial, owing to difficulty in interpreting the true phase behavior. A more valid interpretation on the phase behavior in PLLA/PMMA blends has been recently offered by Li and Woo (40), and they have claimed that the blend systems of s-PMMA/PLLA and a-PMMA/PLLA are immiscible with an asymmetry-shaped upper critical solution temperature (UCST) behavior near 230–250°C. On the other hand, an i-PMMA/PLLA blend remains immiscible up to thermal degradation without showing any transition to UCST upon heating. In addition to the phase behavior in blends, the morphology and nucleation density of PLLA crystals in tactic PMMA/PLLA blends are also affected by the critical temperature of melt treatment (T_{max}) as shown in Figure 2 (40). This figure shows POM micrographs of the spherulites of PLLA blended with various tactic PMMAs melt-crystallized at 130°C from the temperature below UCST (row A) and above UCST (row B). Figure 2**A** shows small and irregular PLLA crystals with many occluded phases, which reflect a mechanism of heterogeneous nucleation. The large-sized PLLA spherulites are observed in Figure 2**B**, indicating that PLLA is crystallized from the single-phase liquid blend (above UCST).

Phase Behavior in Blends of a-, i-, and s-PMMA. Generally polymers with same repeated units but different tacticities (ie, stereoisomers) are not all miscible with each other. Examples are reported in blends of PMMA of different tacticities (41–45). White and Filisko have concluded that a-PMMA and i-PMMA could be one or two phases, as verified by using DSC, with the results depending on sample preparation methods (42). Krause and Roman earlier reported

that a binary blend of i-PMMA and s-PMMA was miscible by using dilatometry analysis (43). However, Bauer and Bletso concluded differently that the i-PMMA/s-PMMA blend system was immiscible, which was based on characterization results of dilatometry, mechanical damping, and torsional modulus (44). Schroeder and co-workers indicated that when i-PMMA and s-PMMA samples were mixed by using comparable molecular weights based on DSC measurements, miscible systems were formed in a whole range of compositions (45). These studies have shown that the phase behavior in blends of PMMAs remains yet unresolved and perhaps may be conflicting based on interpretations by different investigators.

Using optical and scanning electron microscopes, dynamic mechanical analysis, and DSC, effects of tacticity on the phase behavior in three pairs of binary blends comprising any two of i-, s-, and a-PMMAs have been thoroughly studied (46). Miscibility is confirmed in all three binary blends (ie, a-PMMA/i-PMMA, a-PMMA/s-PMMA, and i-PMMA/s-PMMA); however, T_g versus composition relationships for the a-PMMA/i-PMMA blend differed significantly from the other two pairs. Tacticity in PMMA may lead to subtle differences in molecular interactions in the tactic polymers; and in turn such a difference in the interactions results in variation in the glass transition and phase behavior in these three blends. Chang and Woo have reported that miscibility is confirmed more unambiguously for all three pairs of binary blends (a-PMMA/i-PMMA, a-PMMA/s-PMMA, and i-PMMA/s-PMMA), which all exhibit a single, composition-dependent glass transition and a homogeneous phase morphology (46). Figure 3 shows plots of T_g versus composition relationships that differ among the three pairs. By judging from the T_g behavior, the order of interaction in blends as follows: i-PMMA/s-PMMA > a-PMMA/s-PMMA $\gg$ a-PMMA/i-PMMA blends.

Complex Formation in Mixtures of PMMA of Opposite Tacticities. Mixtures of polymers of same structures but opposite chirality are known to form complexes, such as complexes of PLLA and poly(D-lactic acid). Mixtures of polymers of opposite tacticities have also been reported to have capacity of forming complexes. Formation of stereocomplexes between i-PMMA and s-PMMA was first reported by Liquori and co-workers (23). Other factors, such as the polymer concentration (47–49), mixing ratio (50–52), molecular weight (53–55), and solvent effect (56,57) of the stereoregular polymers, also affect formation of stereocomplexes between i-PMMA and s-PMMA. In addition, stereocomplexes composed of tactic PMMAs are known to be produced both in bulk and in solution (51–53). For the solvent effects in blends, three groups of solvents for blending mixtures of i-PMMA and s-PMMA can be classified: complexing, weakly complexing, and noncomplexing types (56,57). Furthermore, the maximum effect of the mixing ratio on the stereocomplex formation is reported to be for mixtures with a weight ratio of (i/s) = 1/2, although other ratios of (i/s) = 2/1 and 1/1 are also reported to induce complexation (50–52,58,59). Various explanations have been proposed for the formation of stereocomplexes between i-PMMA and s-PMMA (60–62). In 1989, a PMMA stereocomplex model was proposed by Schomaker and Challa that the double-stranded helix structure of PMMA stereocomplex was composed of a 9_1 i-PMMA helix surrounded by a 18_1 s-PMMA helix on the basis of x-ray analysis on the stretched fibers (60). More recently, Kumaki and co-workers proposed that a triple-stranded-helix model for PMMA complex structure on the basis of high-resolution AFM analysis (62).

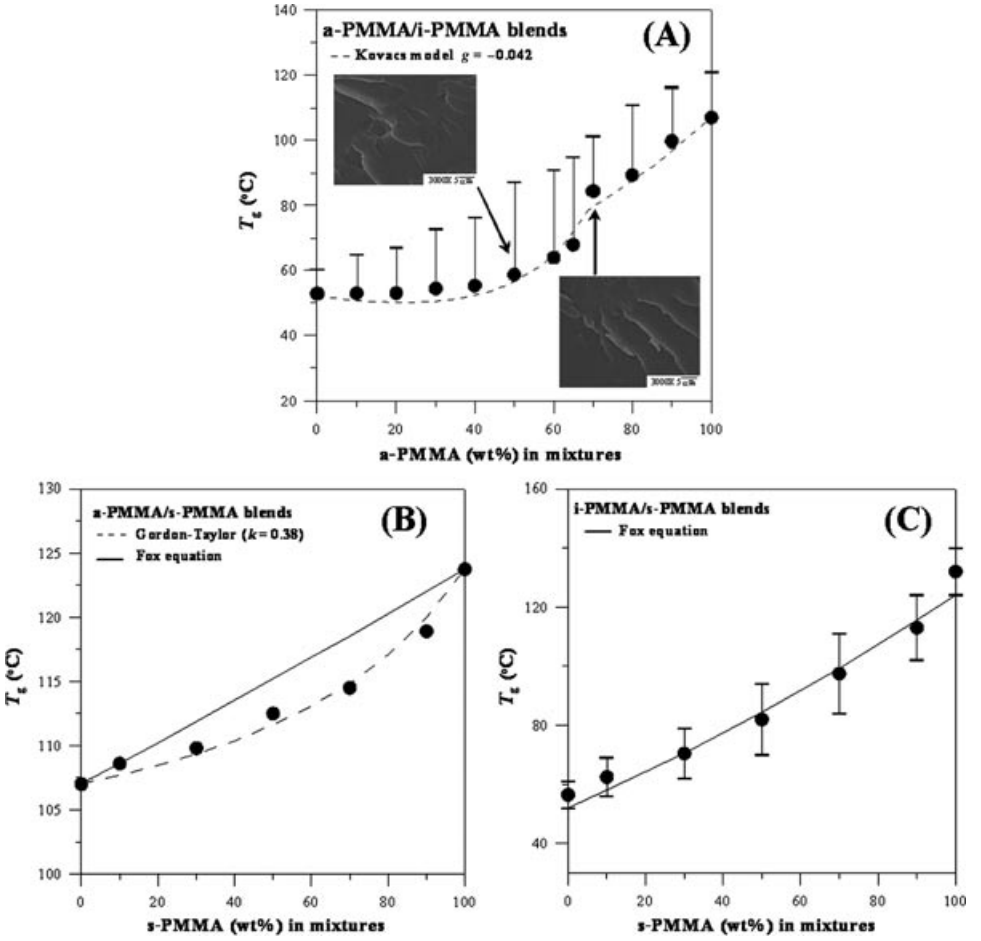


Fig. 3. Plots of T_g versus composition for (A) a-PMMA/i-PMMA (B) a-PMMA/s-PMMA and (C) i-PMMA/s-PMMA blends. Reprinted from Ref. (42) with permission from The Royal Society of Chemistry.

O'Reilly and Mosher were the first to report the conformational energy difference of stereoregular PMMA by using IR spectroscopy (27). The absorbance band at 860 cm^{-1} corresponding to an s-PMMA vibration is stronger in the spectra of the stereocomplex solution in acetonitrile (a complexing solvent) than in the corresponding solution of only s-PMMA, which corresponds to long s-sequences in the extended chain conformation of the backbone (61,63). Earlier, Tretinnikov with Ohta reported that a strong preference of trans–trans backbone conformation both for i-PMMA and s-PMMA; the preference is only slightly higher for s-PMMA. Namely the complexation significantly increases the regularity of torsion angles for the backbone trans state in i-PMMA and *s*-cis → *s*-trans isomerization of ester groups in s-PMMA (64,65).

More recently, the stereocomplex capacity of tactic PMMAs (i-PMMA and s-PMMA) of high molecular weights has been shown to be enhanced by adding a

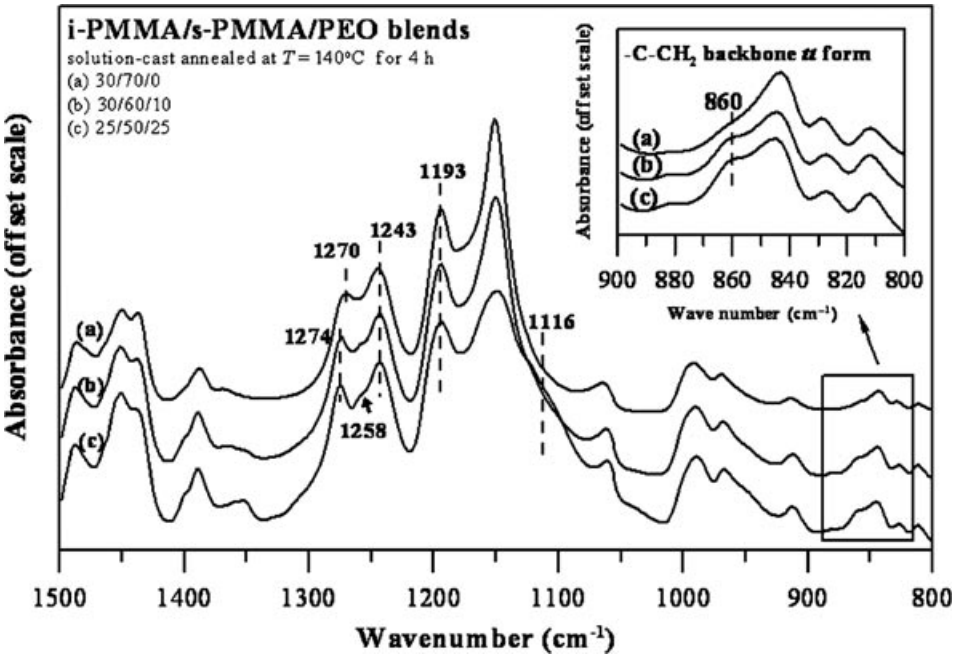


Fig. 4. FT-IR spectra in 1000–1500 cm^{-1} for solution-cast ternary i-PMMA/s-PMMA/PEO blends annealed at 140°C for 4 h. Reprinted from Ref. (62) with permission from the American Chemical Society.

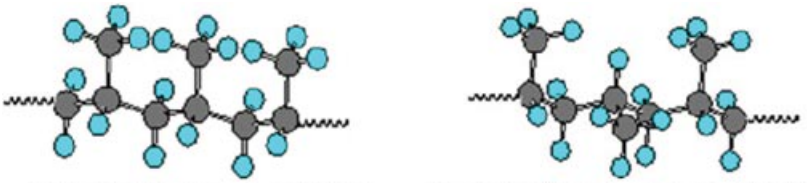
third polymer, which decreases T_g of the originally rigid PMMA chain segments (66). Chang and Woo have reported that a physical interaction or miscibility-enhanced chain entanglement probably exists between PEO and the stereocomplex of tactic PMMAs, leading to stereocomplex formation in the i-PMMA/s-PMMA/PEO ternary blend (66). Figure 4 shows FT-IR spectra in 1000–1500 cm^{-1} for solution-cast ternary i-PMMA/s-PMMA/PEO blends annealed at 140°C for 4 h. The characteristic bands of complexes formation at 1258 and 860 cm^{-1} are clearly observed in a ternary i-PMMA/s-PMMA/PEO blend but are absent in the i-PMMA/s-PMMA blend, indicating that the complexes do form in greater extents via PEO in the blend.

Stereocomplexes of i-PMMA or s-PMMA with diblock- or triblock-copolymer have been reported, such as polyisobutylene block copolymers (67,68), poly(dimethylsi1oxane) block copolymers (69), and polybutadiene (PB) block copolymers (70,71). Yu and Jerome have reported that stereocomplexation of tactic polymers increases the tensile strength of PMMA–PB–PMMA copolymers, containing small s-PMMA blocks at constant molecular weight of PB and i-PMMA, whereas an opposite effect is observed for longer s-PMMA blocks (71).

Tactic Polypropylenes (a-PP, i-PP, s-PP)

Polypropylenes, depending on synthesis routes, can exist in three different tacticities: atactic-, isotactic-, and syndiotactic-PP (a-PP, i-PP, and s-PP). These three

tactic forms of PP have very different physical and mechanical properties. a-PP, of M_w = 12,000, is noncrystalline and amorphous, with T_g = ca –27.2°C (measured with DSC) and density = 0.85 g/cc. i-PP has T_g = –26°C and T_m = 160°C (measured with DSC), and density = 0.9 g/cc. i-PP is known to pack into two crystal cells = α and β forms. The α-form crystal in i-PP is monoclinic with 3/1 helix conformation, whereas the β-form crystal in i-PP is hexagonal cell with same 3/1 helix conformation (72). Syndiotactic polypropylene (s-PP), at M_w = 127,000 and M_n = 54,000 g/mol, has T_g = –4.3°C, T_m = 126°C, and density = 0.9 g/cc. s-PP usually has higher T_g than i-PP, but s-PP has a lower T_m than i-PP. Of these three forms, only i-PP is commercially important as it has a higher melting point than s-PP. Commercially produced PP usually exhibits a mix tacticity composed of mostly isotactic segments with a small percentage of syndiotactic isomers. Their structures with dangling bonds on two ends are illustrated below



Isotactic polypropylene (i-PP) **Syndiotactic polypropylene (s-PP)** (7)

Blends of polymers of same chemical structures but different configurations may have a good likelihood of forming homogeneous mixtures among the stereoisomers, or occasionally even crystalline complexes, but they are not always miscible. Crystalline complex formation in mixtures of i-PP/s-PP has not been reported; the blend miscibility and phase behavior between PPs of different tacticities, however, have been widely studied. Although blends of polypropylenes of different tacticities have been widely studied in the past, there are still on-going debate on the true phase behavior. That is, what is the phase behavior for the blends of PP of different tacticities. It is critical and interesting to probe whether the PP blends show miscibility or immiscibility with UCST. Except for several earlier theoretical predictions based on the Flory–Huggins mean-field theories, UCST behavior had not been experimentally proven for blends of s-PP/i-PP or a-PP/s-PP, owing to interference of the correct interpretation on the phase behavior from PP crystallinity. Semicrystalline polymers with different tacticities (ie, stereoisomers) are not all miscible, which seems a peculiar phenomenon considering that tactic polymers possess identical chemical units differing merely in configurations. For a long time, it has been an intellectually interesting quest that intrigues many investigators probing for answers. A lengthy debate is ongoing whether or not two semicrystalline polymers of same chemical structure but different tacticity are truly miscible in the amorphous state, since they are of the same chemical structure. Further, the problem is compounded by the fact that it is usually difficult to assess precisely the phase behavior or miscibility in mixtures of polymers differing only in tacticity but with closely spaced, or almost the same glass transition temperatures. The phase behavior in melt-state binary blends of tactic polypropylenes (i-PP, s-PP, and a-PP) has long been a difficult

subject because all constituents possess same chemical units with same physical properties other than different crystals at solid state. Note that the blend of two isomers, such as PVAc/PMA, differs from the blend system of two tactic polymers, such as i-PP and s-PP, in that the former is polar and amorphous and T_gs of two constituents are far apart, but the latter is nonpolar and semicrystalline with closely-spaced T_gs, and thus more difficult to interpret the phase behavior. Earlier, Thomann and co-workers have claimed that blends of i-PP/s-PP are immiscible (73,74). In addition, Maier and co-workers (75) have concluded that polypropylenes (PPs) of different tacticities (a, i, or s) are not all miscible with each other. They have concluded that the a-PP/i-PP blend system is miscible, but the a-PP/s-PP system is incompatible with separate phases. Silvestri and Sgarzi (76) have concluded that a-PP is partially miscible with s-PP but immiscible with i-PP, which contradicts with those found by Maier and co-workers (75) or Thomann and co-workers (73,74). Later, Philips (77) also conducted a study on morphology of tactic polypropylene mixtures and reported that the i-PP/a-PP blend has UCST below 155°C and is miscible at a melt state, whereas i-PP/s-PP mixtures exhibit a phase-separated texture at crystallization temperatures. The result of Philips agrees with that of Maier and co-workers, but directly contradicts that of Silvestri and Sgarzi. These findings illustrate unsettled issues on blends of PP. The phase behavior in the i-PP/s-PP blends may be difficult to deal with, owing to extremely fast crystallization of both constituent polymers (i-PP and s-PP). Interpretation of the miscibility or phase behavior at the melt state of the tactic PP mixtures based on morphology of the annealed crystals at crystallization temperature may be misleading, and conflicting views have been presented (73–75,78,79).

Woo and co-workers (80) have utilized novel approaches to construct experimental UCST phase diagrams of blends of tactic PPs by separating the amorphous phase domains from the crystalline spherulites, yielding plausible data for experimentally determining the UCST in s-PP/i-PP blend versus a-PP/s-PP blend, rather than theoretical predictions of phase diagrams. Figure 5 shows the experimental UCST for a s-PP/i-PP blend upon heating to high temperatures above their melting points. Theoretically computed phase diagrams for blends of tactic PPs (75) are also shown in the figure for comparison with the experimentally defined phase diagrams. In addition, the study of Woo and co-workers (80) used the method of equilibrium melting points to estimate the Flory–Huggins interaction parameter for the a-PP/i-PP blend and it has been shown to possess a significantly negative value ($\chi_{12} = -0.21$). This value of interaction strength proves that the a-PP/i-PP blend is indeed miscible in the melted amorphous as well as semicrystalline states, as previously reported in the literature. However, the interaction parameters for the s-PP/i-PP and a-PP/s-PP blends have been found to be nearly zero ($\chi_{12} = -0.02$ and -0.007, respectively, at $T = 150$–180°C), indicating that the interactions in the two latter blends are rather weak and that the corresponding phase behavior for the s-PP/i-PP and a-PP/s-PP blends may border on immiscibility at ambient temperature.

In comparison with blends of nonpolar PP, blends of polystyrenes of three different tacticities (a-PS, i-PS, s-PS) have also been widely studied. The phase behavior and miscibility in blends of PSs of different tacticities have been shown

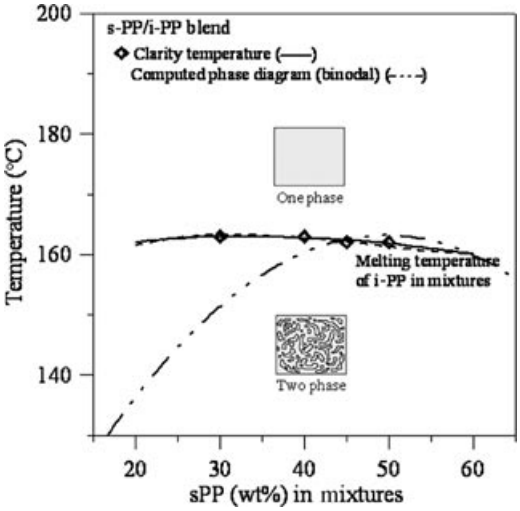


Fig. 5. Experimental UCST diagrams for s-PP/i-PP blends in comparison with theoretical UCST prediction (71). Crystal melting points (for higher melting i-PP) plotted in the graph form. Reprinted from Ref. (76) with permission from the Elsevier.

to differ from those in blends of PPs with different tacticities, perhaps owing to the fact the former ones are more polar in molecular structures but the latter ones are nonpolar possessing only weak van der Waals forces. In addition, the crystallinity in PP blends might have made it more difficult to interpret the miscibility and phase behavior in the amorphous domains. By contrast, the i-PS/s-PS blends, with much lower crystallization rates and higher T_gs than those of PP blends, can be quenched to a fully amorphous state and preserved at ambient for convenient characterization of the phase behavior of the blends at amorphous state. Yeh and co-workers (81) proposed miscibility in the a-PS/i-PS blend system based on results of a crystallization kinetic study; they, however, did not provide more direct evidence other than an analysis of the crystallization kinetics of the blend. s-PS and its blends have been an intensive focus of various studies (82). Ermer and co-workers (83) have tentatively proposed that s-PS and a-PS might be at least partially miscible based on the results of solvent diffusion behavior in the blends. A study has followed up some points and positively proven miscibility in the a-PS/s-PS blend by utilizing examination of the interaction parameter from measurements of the equilibrium melting point from the thermodynamics point of view (84). Interactions between the isomeric polymers, even being miscible, are expectedly low. Earlier, Runt (85) investigated a classically known miscible blend system of a-PS/i-PS (M_w ca 50,000 for both) and found that the polymer–polymer interaction parameter (χ) for the a-PS/i-PS pair is about –0.003, which essentially is zero, indicating very weak interactions between the components. An earlier study has shown that the interaction parameter in the a-PS/s-PS system (84) is similarly a small negative but slightly a greater value ($\chi = \sim -0.1$) than that for the a-PS/i-PS system studied by Runt (85). The phase behavior of blends of different tactic polymers is influenced by the structural parameters

such as tacticity, chain polarity, and size of pendant groups. It is of interest to compare the phase behavior and miscibility in various blend systems of polymers differing only in types of tacticities. For the case of polystyrenes with a relatively bulky pendant group and more polar by nature, the miscibility in blends of tactic polymers has been proven to be independent of tacticity in polystyrene. On the other hand, for polypropylenes with a less bulky $-CH_3$ pendant group (ie, lower T_g and faster crystallizing), and less polarity and higher crystallinity (than polystyrenes), the miscibility and phase homogeneity in binary tactic PP blends are more influenced by tacticity in PP. In general, there seems no single rule for predicting the phase behavior in blends composed of polymers of same chemical structures differing only in tacticity, especially when more phenomenal factors are present to influence the phase behavior and intermolecular interactions.

Tactic Polystyrenes (a-PS, i-PS, s-PS)

In contrast to i-PP being the most widely used commercial plastic among the three tactic forms of PP, a-PS is the most useful one among the three tactic configuration, owing to its high enough T_g ($\sim$100°C) of a-PS even though it is fully amorphous and does not have any crystallinity. In fact, a-PS is one of the most widely used plastics for almost 50 years since its first commercialization. Two tactic forms of PS, semicrystalline i-PS and s-PS, were latecomers in comparison to atactic PS. Unlike i-PP being a useful commercial product among the three tactic forms of polypropylenes, the isotactic form of PS (i-PS), however, has little commercial applications, owing to the much lower T_g and not high enough crystallinity in i-PS in comparison to s-PS. Not until its successful commercial synthesis via stereospecific polymerization in as early as 1985 (82,86,87), s-PS was increasingly studied. A structural difference of tacticity leads to variation in crystal packing. i-PS is packed into a trigonal crystal cell with 3/1 helical conformation, but s-PS is known to packed into several crystal forms (or called modifications) depending on thermal or solvent treatments. Unique to s-PS is its polymorphism in crystal cell types under different thermal histories. Most other semicrystalline polymers possess only one type of unit crystal cell; for others, polymorphisms with two crystal cells are known to exist. s-PS exhibits complex polymorphism (88–92) and multiple melting endotherms in association with crystal cells or lamellar patterns (93–98). Generally speaking, four crystal forms (α, β, γ, and δ) in thermal- or solvent-treated s-PS are known (99–103). A combination of α'' and β' crystals is produced when melt-crystallized at low temperatures and the fraction of β'-type crystal increases with successive increases of isothermal temperatures (89,90). Only $\beta(\beta')$-type crystal is generated in s-PS if melt-crystallized at high temperatures above 260°C with no α crystal (neither α' nor α''). Melt-crystallization of s-PS is known to pack into a mix of two common crystal cells: α and β-forms. The α-form s-PS is hexagonal and is favored kinetically, whereas the more stable β-form s-PS is an orthorhombic cell with a zig-zag planar conformation. The relative fraction of α''- and β'-type crystals can be influenced as a function of isothermal melt-crystallization temperatures. In addition, the maximum melting temperatures erasing thermal history and the residence

time in the melt also have a significant effect on the polymorphism of s-PS (98). Furthermore, the polymorphism state of s-PS can be altered in the presence of other miscible polymers: for example, poly(*2*,*6*-dimethyl-*p*-phenylene oxide; PPO) or atactic polystyrene (a-PS) (104–106). Both the α''- and β'-type crystals are observed in the neat melt-crystallized s-PS; however, only the β'-crystal is found in miscible s-PS/a-PS or s-PS/PPO when crystallized at the same conditions. Apparently, blending with the miscible amorphous polymer reduces the possibilities of the formation of α-type crystal in s-PS. In addition, cold-crystallization (in contrast with melt-crystallization) has a dramatically different effect on the polymorphism of s-PS (107–110). Only the α-type (containing two modifications α' and α'') crystal with no β-type crystal generates if s-PS cold-crystallized from its amorphous glassy state. Many studies investigated phase transformation in s-PS by using FT-IR and/or Raman spectroscopy, DSC, and x-ray analysis, and so on (111–120). Correlations between the polymorphism and multiple melting endotherms have been an interesting subject of studies. Coexisting α''- and β'-type crystals (or other additional crystal forms) inevitably lead to multiple melting peaks upon scanning; moreover, the presence of polymorphic crystals in s-PS can further complicate the melting and thermal behavior. Interpretation of the phase transition (transformation between different crystals) may be additionally complicated by a phenomenon of multiple-melting behavior in s-PS.

Synthesis of tactic polystyrene and its structure/property have been two main focuses of s-PS. Synthesis of s-PS requires specific catalysis. In the past decade, since the successful commercialization in 1985 of s-PS, a review article on synthesis and catalysis of s-PS appeared in 1996 by Po and Cardi co-workers (121). Another review article in 2001 by Woo and co-workers (122) dealt with the polymorphism of crystals, multiple melting, spherulite morphology, and miscible blends with s-PS. The article summarizes many useful references on the subject in the 10 years between 1991–2000. Four crystal types (α, β, γ, δ) and some mesophases/submodifications have been identified in s-PS. The α and β forms are the main crystal packing in thermally processed s-PS, whereas the γ and δ crystals are identified only in the solvent-treated s-PS. The δ and γ forms in the solvent-treated s-PS are of a monoclinic crystal cell (with helical chain conformation), and the cell dimensions depend on the types and amount of residual solvent that may be trapped in the crystal. The δ and γ-crystals in the solvent-treated s-PS are more like mesophases that transform readily to the α, β'', or β' crystals upon heating the solvent-treated s-PS to high temperatures near melting. The melt-crystallized α and β crystals in s-PS are the main subject related to the thermal behavior, crystal structures, thermodynamics, kinetics, and stability of these two major crystal packing (α vs β) in s-PS. Analyses of melting behavior, diffractograms, or IR spectra, and so on of s-PS can be complicated by the presence of coexisting polymorphic crystals. In general, a total of four melting peaks (labeled as P-I, P-II, P-III, and P-IV from low to high temperatures) have been identified in a melt-crystallized s-PS that typically contains mixed fractions of both crystals. By refining the techniques of obtaining s-PS with individually isolated α- or β-crystals, recent studies have been able to correct suspected inaccuracy of some thermodynamic and kinetic measurements in earlier studies and to interpret the relative stability of the various crystals in s-PS. s-PS samples could be prepared

so that they contained purely isolated α or β crystal, and the individual crystal types are used for more precise characterization for analysis. The P-I and P–III melting peaks are attributed the β' crystal, whereas P-II and P-IV are attributed to the α'' type. In addition, kinetic and thermodynamic characterizations have been thoroughly performed on individually isolated crystal types (122) and reveal that the α crystal of s-PS has a lower melting temperature than the β crystal, with $T_{m,\alpha}{}^{\circ} = 281.7^{\circ}$C, but $T_{m,\beta}{}^{\circ} = 288.7^{\circ}$C. The crystallization kinetics of the α-crystal is a heterogeneous nucleation with higher rates, whereas the β crystal is a homogeneous nucleation with lower rates. The β' type is more thermodynamically stable than the α'' type. but the α'' type is kinetically more favorable. Both α to β crystals are stable solids, and transformation between them can only be achieved by melting and repacking, but not by solid–solid transformation. Nevertheless, the individual melting/reorganization of these two crystals might undergo crystal transformation via the solid–liquid–solid transition. The crystallization kinetics of β' crystal is a homogeneous nucleation and lower rates. By comparison, crystallization kinetics of the α crystal is a heterogeneous nucleation and higher rates. Microscopy characterization also revealed a highly nucleated crystallization of the α crystal. The effect of blend miscibility on the polymorphism behavior in s-PS is also discussed. Effects of miscibility on polymorphism in s-PS have been investigated by studying two miscible blends of s-PS/a-PS or s-PS/PPO (104–106). Both miscible blends containing s-PS have been found to favor growth of β crystal than neat s-PS when subjected to the same melt-crystallization conditions.

The γ and δ crystals are less encountered and usually involved only in solvent treatments of s-PS; melt-crystallization of s-PS usually leads to the α-type (a hexagonal or trigonal unit cell) and β type (an orthorhombic cell) commonly seen in bulk s-PS subjected to thermal treatments (annealing, cooling from molten state, isothermal cold- or melt-crystallization). The α crystal in s-PS has a lower melting temperature ($T_{m,\alpha}{}^{\circ} = 281.7^{\circ}$C) than the β crystal ($T_{m,,\beta}{}^{\circ} = 288.7^{\circ}$C). The heats of fusion measured at the respective maximum crystallinity are also different between these two crystals: $\Delta H_{f,\alpha} = 27.9$ J/g for the α crystal, which is lower than $\Delta H_{f,\beta} = 31.5$ J/g for the β crystal, at the respective maximum crystallinity. The results suggest that the β' type is more thermodynamically stable than the α'' type; therefore, when crystallized at higher temperatures closer to the equilibrium melting, β' crystal is the preferential species. In addition, molecular weights in polymers may affect the polymorphism in s-PS. Using s-PS of a low molecular weight ($M_w = 63{,}000$), it has been found to develop only a β-type unit cell upon melt crystallization at all temperatures (122). A correlation between the lamellar morphology and multiple-melting behavior in the s-PS has been demonstrated by using the sole β-form crystalline s-PS ($M_w = 63{,}000$). When crystallized at lower temperatures (250°C or lower), the β-form s-PS displays three multiple melting peaks (ie labeled as P-I, -II, -III) and the spherulitic morphology is composed of two main crystalline domains, which are initially thin and straight lamellar bundles (P-1) and eye-like lamellae platelet crystal (P-II). The P-III crystal was not initially present in significant extent in s-PS crystallized at low temperatures. However, upon scanning to higher temperatures, the initially thinner flat-on lamellae (P-I) are melted and then immediately repacked to more thickened and branched lamellae (P-III), whose orientation is also twisted from the original flat-on to an edge-on (perpendicular to substrate) pattern. Detailed

mechanisms of transformation between P-I and P-III crystals via melting/repacking are evident. P-III lamellae could also be directly developed in s-PS by melt-crystallization at higher temperatures (260°C), whereas P-I and P-II crystals were absent. Only the P-III crystal (branched, thick, axialite) exists in the s-PS melt-crystallized at 260°C or above (123). In addition, polymorphism in s-PS may be influenced by cold- or melt-crystallization, which, respectively, is the crystallization from a glassy and melt state of the polymer. Melt-crystallization in s-PS usually produces mixed fractions of both α- and β-form crystals, except for low-M_w s-PS that melt-crystallizes into predominantly β-form crystal. A study by Sun and Woo (110) has pointed out that cold-crystallization of s-PS produces only the α-type unit cell packed into crystalline domains of different spherulitic morphology patterns. The morphology contains a granular-spherulitic texture when cold-crystallized at low temperatures, whereas high-temperature cold-crystallization produces additional sheaf-like lamella radiating out from the central spheres.

In summary, tacticity in polymers has been discussed via examples of three common and commercially important vinyl polymers: PMMA, PP, and PS. Other vinyl polymers may also be synthesized to specific tactic forms or an atactic type depending on stereospecific catalysts. Tacticity in polymers influences the structures, morphology, and properties of the polymers. However, polymers do not always have to be in tactic forms to have desirable use properties. PMMA and PS are commercially important in their atactic forms; by contrast, PP has to be in the isotactic form to be commercially attractive. Atactic polymers are mostly amorphous and noncrystalline; tactic polymers, either syndiotactic or isotactic form, are crystallizable. But in general, different tacticity in polymers of same chemical structure results in different crystal unit cell and different T_m, T_g, and physical properties. Mixtures of polymers of opposite tacticity (syndiotacticity and isotacticity), unlike mixtures of polymers or compounds of opposite chirality, do not always form stereocomplexes. Only the mixtures of i-PMMA and s-PMMA have been shown to yield weak stereo-complexing capacity, but s-PP/i-PP or s-PS/i-PS blends have not been known to result in stereocomplexes. This may be easy to comprehend as structurally the isotacticity and syndiotacticity forms are not mirror images to each other, unlike the chiral compounds.

Tactic polymers may be mixed or compounded into blends. Blends of polymers of same chemical structure but opposite tacticities (isotacticity and syndiotacticity) are not always miscible. A blend of i-PMMA with s-PMMA is miscible, and so is the blend of i-PS with s-PS, but a blend of nonpolar and highly crystalline s-PP with i-PP shows immiscibility with the UCST behavior. In addition, as variation of tacticity in tactic polymers results in a difference in microstructures, and thus may influence intermolecular interactions with other polymers. For examples, blends of s-PMMA/PLLA and a-PMMA/PLLA are immiscible with an asymmetry-shaped UCST behavior near 230–250°C; on the other hand, i-PMMA/PLLA blend remains immiscible up to thermal degradation without showing any transition to UCST upon heating to ~300°C. In blends with the borderline phase homogeneity, the tacticity effect on miscibility is more pronounced. This is exemplified in the case that isotactic PVME (i-PVME) is shown to be less miscible with atactic PS (a-PS) than syndiotactic PVME (s-PVME) with the same a-PS. Conversely, in blends with evident intermolecular interactions, the effect of

tacticity on the phase behavior is less critical or minimal. The classical miscible blend of a-PS with PPO is one example. The blend of i-PS/PPO is also miscible like the a-PS/PPO blend, so it is a blend of s-PS/PPO.

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