Chapter 1   Introduction

1.1   Atom Transfer Radical Polymerization

With regard to the fast development of materials science, the use of polymeric materials has been so extensive that the design of proper polymeric materials at the molecular level has become very important. The synthesis of polymers with well-defined compositions, architectures and functionalities has been a rapidly growing research area. In this context, controlled/living radical polymerization systems [1, 2], such as atom transfer radical polymerization (ATRP) [3], radical polymerization with reversible addition-fragmentation chain transfer (RAFT) [4], and the nitroxide-mediated polymerization (NMP) [5], have been extensively studied.

ATRP was reported simultaneously by two groups: (1) Matyjaszewski et al. [6] and (2) Sawamoto and coworkers [7] since 1995. The ATRP process that Matyjaszewski et al. developed out was to utilize a Cu (I)/bipyridine complex as a halogen transfer agent that function between dormant and active polymer chains. Besides, the ATRP reaction reported by Sawamoto and coworkers uses a system consisting of reversible and hemolytic cleavages of carbon-halogen terminal groups assisted by transition metal complexes.
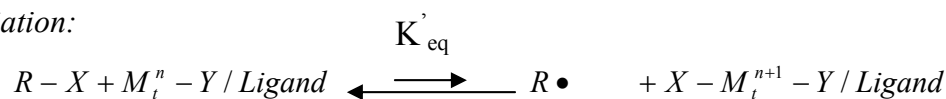
1.1.1 Mechanistic Understandings of ATRP

A general mechanism for ATRP shows in Scheme 1.1. The active species are generated through a reversible redox process catalyzed by a transition metal complex (M_t^n-Y/Ligand, where Y may be another ligand or the counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, R-X.
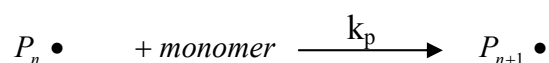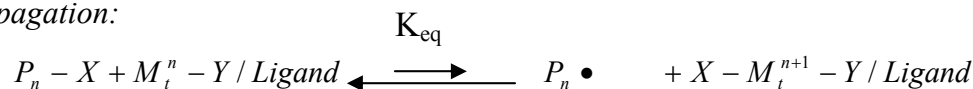
This process occurs with a rate constant of activation, k_{act}, and deactivation, k_{deact}. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) determines the polymerization rate. ATRP will not occur or occur very slowly if the equilibrium constant is too small. In contrast, too large an equilibrium constant will lead to a large amount of termination because of a high

radical concentration [8]. Each monomer possesses its own intrinsic radical propagation rate.
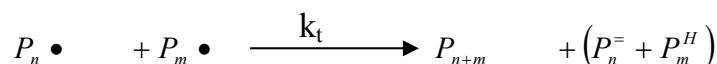
Initiation:

$$R - X + M_t^n - Y / Ligand \xleftrightarrow{\quad K'_{eq} \quad} R\bullet \quad + X - M_t^{n+1} - Y / Ligand$$

$$R\bullet \quad + monomer \xrightarrow{\quad k'_p \quad} P_1\bullet$$

Propagation:

$$P_n - X + M_t^n - Y / Ligand \xleftrightarrow{\quad K_{eq} \quad} P_n\bullet \quad + X - M_t^{n+1} - Y / Ligand$$

$$P_n\bullet \quad + monomer \xrightarrow{\quad k_p \quad} P_{n+1}\bullet$$

Termination:

$$P_n\bullet \quad + P_m\bullet \xrightarrow{\quad k_t \quad} P_{n+m} \quad + \left(P_n^= + P_m^H \right)$$

Scheme 1.1. *General mechanism for ATRP.*

Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p. Termination reactions, k_t, also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, X-M_t^{n+1}, as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination [9]. A successful ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

1.1.2 Typical Phenomenology for ATRP

1. Kinetics

The kinetics of ATRP is discussed here using copper-mediated ATRP as an example. According to Scheme 1.1 using the assumption that contribution of termination becomes

insignificant due to the persistent radical effect (PRE) [9] (especially for the chain-length-dependent PRE [10]) and using a fast equilibrium approximation, which is necessary for observed low polydispersities, the rate law (Eq. (1)) for ATRP can be derived as follows.

$$R_p = k_p[M][P^*] = k_p K_{eq}[M][I]_0 \times [Cu^I]/[X\text{-}Cu^{II}] \qquad (1)$$
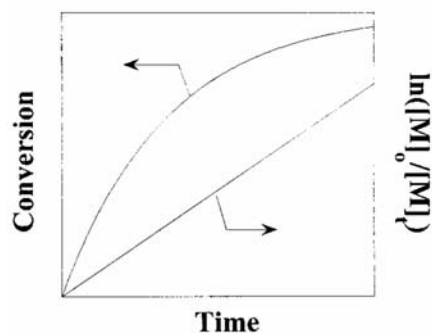

Figure 1.1. *Schematic representation of the dependence of the conversion on time in linear and semilogarithmic coordinates.*

Figure 1.1 shows a typical linear variation of conversion with time in semilogarithmic coordinates. Such a behavior indicates that there is a constant concentration of active species in the polymerization and first-order kinetics with respect to monomer. However, since termination occurs continuously, the concentration of the Cu (II) species increases and deviation from linearity may be observed. For the ideal case with chain length independent termination, PRE kinetics implies the semilogarithmic plot of monomer conversion vs. time to the 2/3 exponent should be linear [9]. Nevertheless, a linear semilogarithmic plot is often observed. This may be due to an excess of the Cu (II) species present initially, a chain–length-dependent termination rate coefficient, and heterogeneity of the reaction system due to limited solubility of the copper complexes. It is also possible that self-initiation may continuously produce radicals and compensate for termination [11]. Similarly, external orders with respect to initiator and the Cu (I) species may also be affected by the PRE [12].

2. Molecular Weight and Distribution

Similarly to a typical living polymerization, the average molecular weight of the

polymer made by a well-controlled ATRP can be predetermined by the ratio of consumed monomer and the initiator ($DP_n = \triangle[M]/[I]_o$, DP = degree of polymerization) while maintaining a relatively narrow molecular weight distribution ($1.0 < M_w/M_n < 1.5$). The molecular weight distribution or polydispersity (M_w/M_n) is the index of the polymer chain-length distribution. Eq. (2) illustrates how the polydispersity index in ATRP in the absence of significant chain termination and transfer relates to the concentrations of initiator [RX], deactivator [D], k_p, k_{deact}, and the monomer conversion (p) [13].

$$M_W / M_n = 1 + \left(\frac{[RX]_0 k_p}{k_{deact}[D]} \right)\left(\frac{2}{p} - 1 \right) \qquad (2)$$

This equation holds for conditions when initiator is completely consumed and degrees of polymerization are sufficiently high; otherwise the Poisson term should be added ($1/DP_n$).

In addition, well-defined polymers with molecular weights ranging from 1,000 to 150,000 have been successfully synthesized. However, termination and other side reactions are also present in ATRP, and they become more prominent as higher molecular weight polymers are targeted. For example, in the copper-mediated ATRP of styrene, a slow termination process was observed arising mainly from the interaction of the Cu (II) species with both the growing radical and the macromolecular alkyl halide. This effect is negligible for low molecular weight polystyrene but could result in an upper limit to styrene ATRP [14].

1.1.3 Composition for ATRP

1. Monomers

Various monomers have been successfully polymerized using ATRP: styrenes, (meth)acrylates, (meth)acrylamides, dienes, acrylonitrile, and other monomers which contain substituents that can stabilize the propagating radicals (Figure 1.2). Ring-opening polymerization is also possible. However, even using the same catalyst under the same conditions, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. The product of k_p and K_{eq} essentially determines the polymerization rate.

ATRP will occur very slowly if the equilibrium constant is too small. This is plausibly the main reason why polymerization of less reactive monomers such as olefins, halogenated alkenes, and vinyl acetate has not yet been successful. Because each monomer has specific equilibrium constant, optimal conditions for polymerization which include concentration and type of the catalyst, temperature, solvent, and some additives may be quite different.
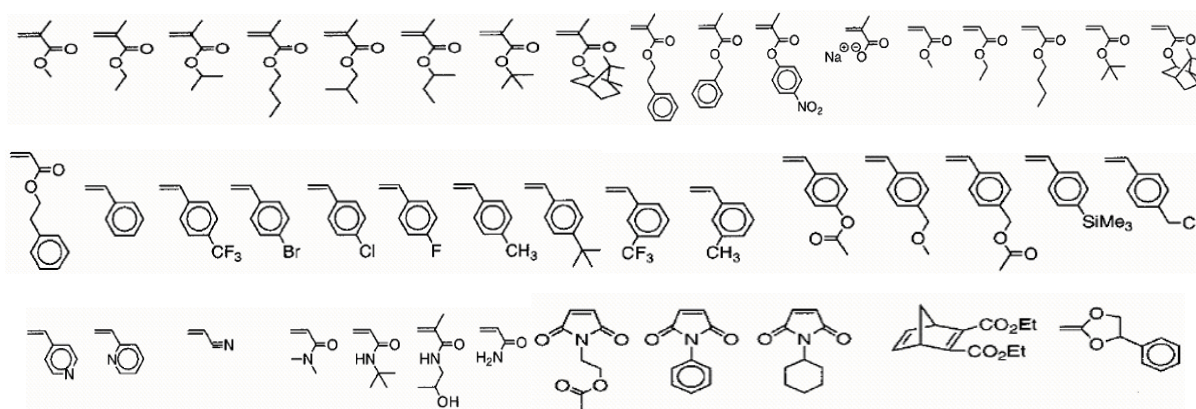

Figure 1.2. *Monomers for ATRP.*

2. Initiators

The role of the initiator in metal-catalyzed living radical polymerization is to form an initiating radical species via homolytic cleavage of its labile bond such as C-halogen by the metal catalysts. In most cases, the dissociated halogen is subsequently reattached to the propagating radical chain end to give a dormant species. A variety of initiators have been used successfully in ATRP, such as halogenated alkanes, benzylic halides, α-haloesters, α-haloketones, α-halonitriles, and sulfonyl halides (Figure 1.3).

Two parameters are important for a successful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of side reactions should be minimized. Also, there are several general considerations for the initiator choice. (1) The stabilizing group order in the initiator is roughly CN > C(O)R > C(O)OR > Ph > Cl > Me. (2) The general order of bond strength in the alkyl halides is R-Cl > R-Br > R-I. Thus, alkyl chlorides should be the least efficient initiators and alkyl iodides the most efficient. However, the use of alkyl iodides requires special precautions.
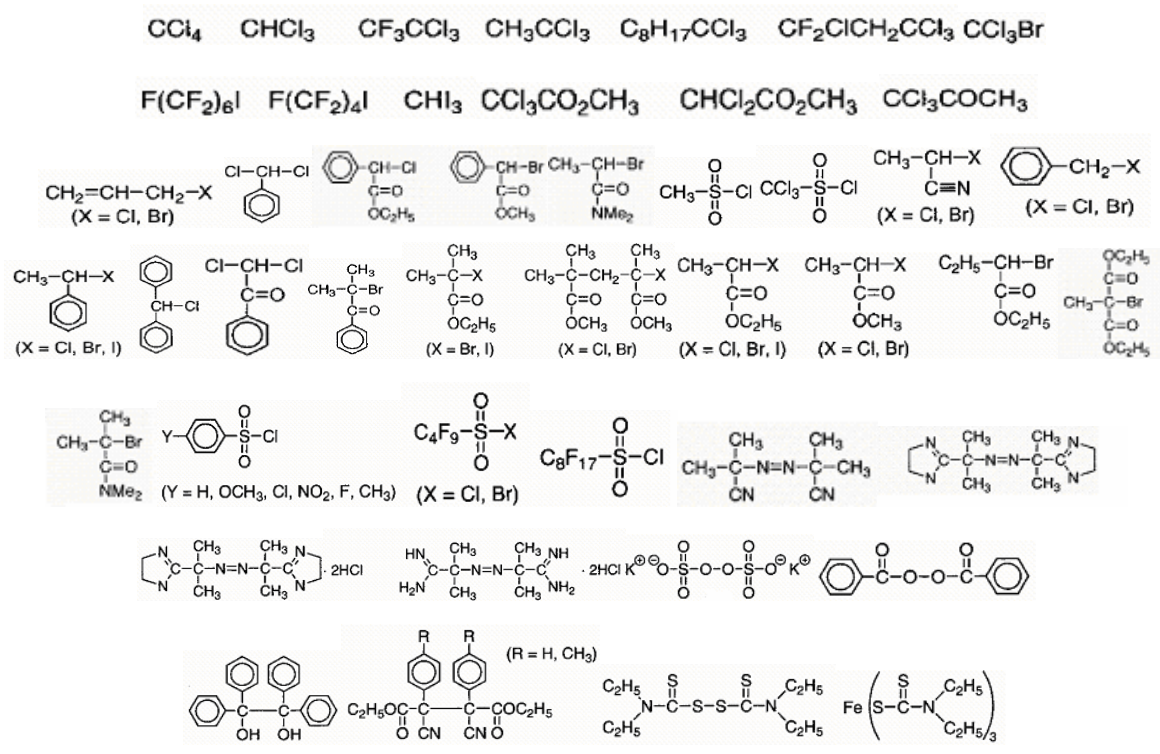
Figure 1.3. *Iinitiators for ATRP.*

3. Transition-Metal Complexes

A number of transition metal complexes have been applied in ATRP, such as Mo, Re, Ru, Al, Fe, Rh, Ni, Pd, and Cu (Figure 1.4).
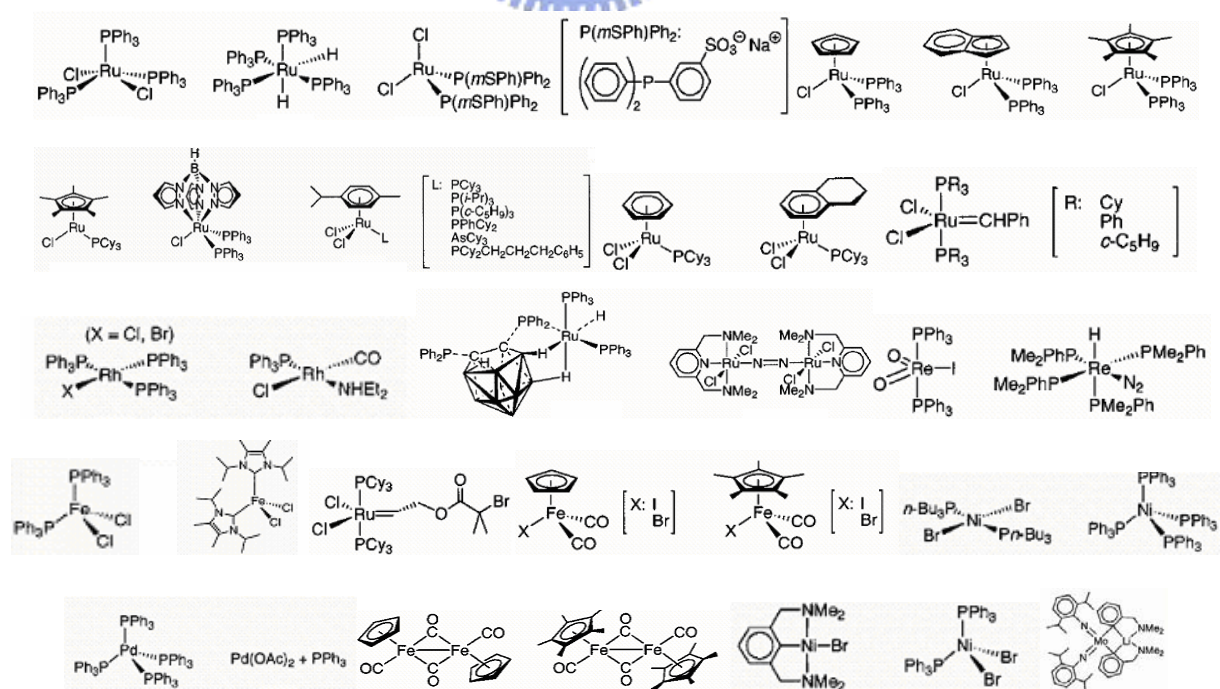

Figure 1.4. *Metal catalysts for ATRP.*

The metal center should undergo an electron transfer reaction with the abstraction of a (pseudo)halogen and expansion of the coordination sphere. In addition, to differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species. Currently, complexes of late and middle transition metals are most efficient catalysts for ATRP. However, catalytic activity and selectivity is strongly ligand dependent. This is possible by careful design of ligands, which dramatically increase selectivities and also activities of the involved complexes. Since ATRP is very often used for polar monomers, early transition metals may be deactivated by (meth)acrylates due to their high oxophilicity and perhaps weaker halogenophilicity. They may also form direct bonds to carbon and abstract β-hydrogens. However, some ligands may provide high selectivity for halogen transfer over other pathways.

4. Ligand

The main role of the ligand in ATRP is to solubilize the transition-metal salt in the organic media and to adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer, such as sulfur ligands, oxygen ligands, nitrogen ligands, phosphorous ligands and so on (Figure 1.5).
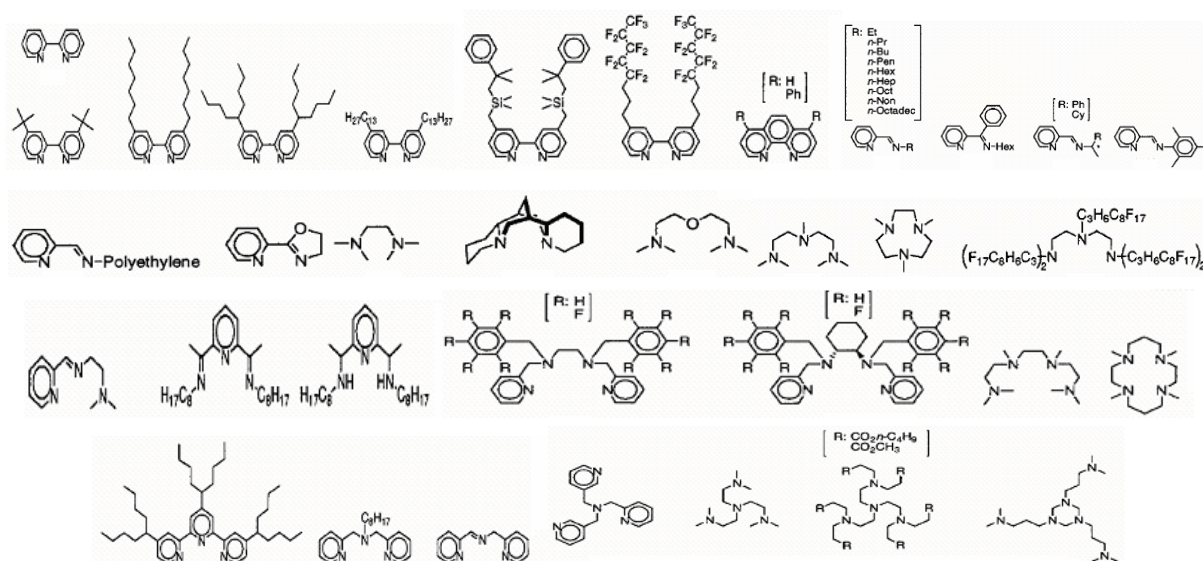

Figure 1.5. *Ligands for copper catalysts.*

It has been reported that nitrogen ligands have been used in copper- and iron-mediated ATRP. For copper-mediated ATRP, nitrogen-based ligands work particularly well. In contrast, sulfur, oxygen, or phosphorus ligands are less effective due to inappropriate electronic effects or unfavorable binding constants. Furthermore, the electronic and steric effects of the ligands are important. Reduced catalytic activity or efficiency is observed when there is excessive steric hindrance around the metal center or the ligand has strongly electron-withdrawing substituents.

1.1.4 Applications of ATRP

While the advent of ATRP is relatively recent—the first publication was in 1995—the number of contributions with regard to materials synthesized at least in part using this technique is quite large. Many new functional polymers with novel and controlled compositions and topologies have been prepared by ATRP, and a complete structure-property relationship has to be developed to allow a correlation of molecular structure with macroscopic properties, which were schematically represented in Figure 1.6.
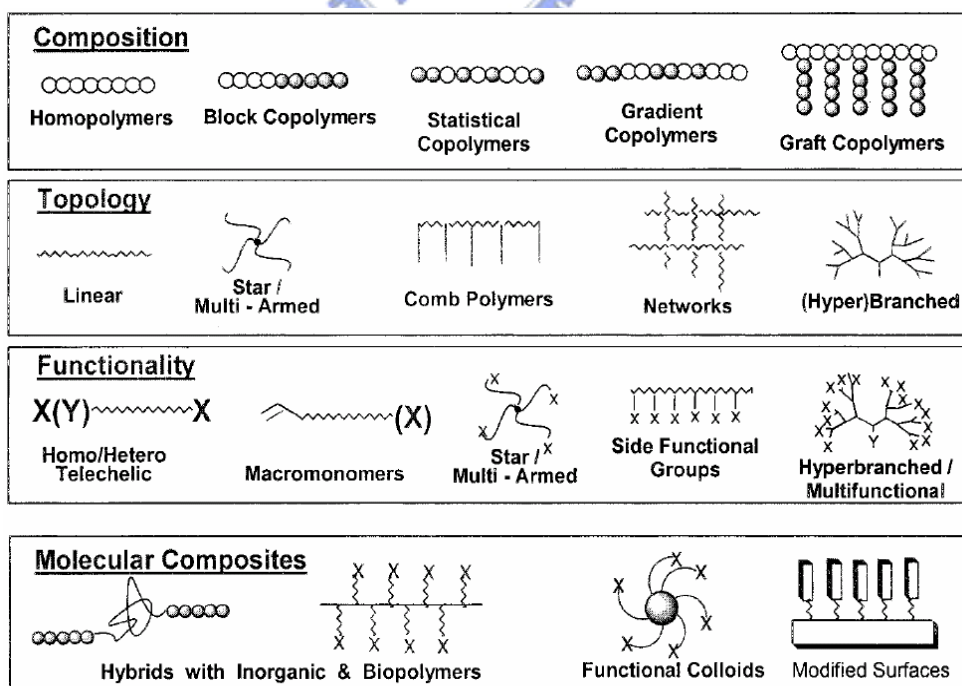

Figure 1.6. Schematic representation of controlled topologies, compositions, functionalities and molecular composites prepared by ATRP.

Regardless, the development of ATRP techniques should have a tremendous impact on the range of commercial products prepared by a free radical method. Patent activity indicates market targets include coatings, adhesives, elastomers, sealants, lubricants, imaging materials, powder binder compositions, pigment dispersants, personal care compositions, detergents, water treatment chemicals, and telechelic materials with hydroxy, epoxy, carboxy, and amine functionality in addition to amphiphilic block copolymers. Higher value applications include photopaternable materials and biological sensors.

In summary, ATRP is a valuable tool for the design and synthesis of novel materials. The polymers can be prepared under facile reaction conditions, using a multitude of available polymerizable monomers with accessible chain functionalities. The types of materials produced by ATRP will be limited only by the imagination of those generating the materials.

1.2   *Polymer Miscibility and Interaction*

Polymer blend phase behavior can be predicted or analyzed by inserting the binary interaction model into the thermodynamic framework of either the Flory-Huggins theory or an appropriate equation-of-state theory. It is useful for evaluation of isothermal phase boundaries, miscibility maps, or phase separation by using the simplicity of the Flory-Huggins theory and equation-of-state. Recently, several polymer theoretical equation of state are available [15, 16], and some have been applied to polymer solutions and blends [17, 18]. However, the role of polymer interaction in determining the phase behavior of polymer blends is fascinating from a number of concentrations. Polymer interactions are usually meaning "strong," specific, and orientation dependent. In polymer blends, most it has been widely concerned with the following intermolecular or inter-segment forces:

   a) Strong dipoles

   b) Hydrogen bonds

   c) Charge transfer complexes

   d) Ionic interactions in ionomers

Although a few studies of miscibility in blends where polymer segments interact through charge transfer compolexes and ionic forces have appeared, by far the most common and important systems involving strong interactions are (at the time of writing) those involving hydrogen bonds and/or strong dipole interactions. Hildebrand and Scott considered that molecules with "dipoles capable of forming hydrogen bonds or bridges–are so exceptional in their behavior as to require separate consideration." We concerned with miscibility in polymer mixtures that is a result of hydrogen bond formation.

Polymer miscibility is based on the assertion that the free energy of mixing can be written in the following form:

$$\frac{\Delta G_m}{RT} = \frac{\Phi_A}{M_A}\ln\Phi_A + \frac{\Phi_B}{M_B}\ln\Phi_B + \chi\Phi_A\Phi_B + \frac{\Delta G_H}{RT} \qquad (3)$$

The segmental interaction parameter χ is assumed to represent "physical" forces only, while the ΔG_H term reflects free energy changes corresponding to specific interactions, most commonly, but not necessarily, hydrogen bonds. Nevertheless, hydrogen bonds are not easily characterized. There are two common experimental ways being able to characterized hydrogen bonds within polymers:

a) Thermodynamic: Measurements depend upon thermodynamic changes in a system as a whole and can be related to molecular properties through the analyses of statistical mechanics, and these results are often model dependent and sensitive to the various assumptions that have to be made.

b) Spectroscopic: Spectroscopic techniques can aid in the evolution of miscibility, specifically when the interaction induce a change in the material physical properties (e.g. glass transition temperature); such as a change can be measured by radiative energy, including spectroscopy of solid-state or liquid nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FT-IR), Raman, XPS and others.

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