On the Structural Origin of the Thermochromic Behavior of Urethane-Substituted Poly(diacetylenes)

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ABSTRACT: FTIR spectra recorded during the thermochromic transition of poly-ETCD revealed that, in contrast to some urethane-substituted poly(diacetylenes) containing more flexible side groups, the transition occurs without significant disruption of the hydrogen bonded network of the side groups. The thermochromic behavior of this material was found to be related to a local disordering and reorganization of the methylene segments of the side groups, which allows the conjugated backbone to relax to a less planar conformation. Complete relaxation to a highly deformed, nonplanar conformation is prevented by the retention of the hydrogen bonded lattice, which partially restricts the torsional mobility of the backbone.

Introduction

The thermochromic behavior exhibited by poly(diacetylenes) substituted with urethane containing side groups (R) is well-known, and a substantial effort has been directed toward gaining an understanding of the origins of these unusual, often reversible color changes. For example, in the case of the poly(diacetylenes) in which R = $(CH_2)_nOCONHCH_2COOC_4H_9$ (commonly referred to as poly(nBCMU)), it has been demonstrated that dramatic reversible energy shifts in the optical spectra of solutions,[1] thin films, and crystals[2] of these materials can be induced by suitable changes in solvent environment (solutions) and temperature (solutions and solid materials). For poly(nBCMU), these chromic transitions have been linked to changes in the extent of hydrogen bonding of the side groups.[1-3] Here it is believed that the formation of intramolecular hydrogen bonds stabilizes a more planar conformation of the conjugated backbone, allowing its π-electrons to be delocalized over greater distances along the chain. Disruption of these highly directional secondary bonds, for example via thermal means, results in a less planar backbone conformation and more localized π-electrons. Thus, the thermochromic transitions of poly(nBCMU) are proposed to be due to an order-disorder transition involving extensive hydrogen bond disruption within the side groups. The disorder created by this process is readily observed in the high-temperature phase of these materials by visible spectroscopy in which spectra typically display very broad, ill-defined absorption bands in the wavelength region below 550 nm, characteristic of a highly deformed conjugated backbone with limited interchain interactions.

On the basis of the behavior of poly(nBCMU), one might assume that thermal dissociation of hydrogen bonds in urethane-substituted poly(diacetylenes) is a necessary requirement for reversible thermochromism in these materials. However, as will be discussed in this paper, certain urethane-substituted poly(diacetylenes) containing less flexible or entropically "active" side groups exhibit reversible thermochromic transitions that do not involve the thermal disruption of hydrogen bonds. In addition, these transitions occur without significant loss in crystallinity of the material and with some level of structure maintained in their absorption profiles above the transition temperature. Examples of such urethane-substituted poly(diacetylenes) with R = $(CH_2)_4OCONHX$ include poly-ETCD[4] in which X = CH_2CH_3 and poly-IUPDO[5] in which X = $CH(CH_3)_2$. In addition to these more conventional urethane-substituted poly(diacetylenes), we have recently shown[6] that certain segmented polyurethanes containing poly(diacetylene) chains within their crystalline phase-separated hard-segment domains also exhibit reversible thermochromic behavior. In this case, the side groups are actually polymer chains but the sequence of atoms closest to the conjugated backbone is very similar to the above named polymers. For example, for the thermochromic polyurethane-diacetylene segmented copolymer referred to as HDI-5,7-1000, the atoms nearest to the backbone are R = $(CH_2)_4OCONH(CH_2)_6$. This particular copolymer is unique for two reasons. First, although the thermochromic transition is reversible up to about 130 °C, if the material is heated above this temperature, it is possible to irreversibly lock in its higher temperature phase. Second, at room temperature, this newly formed yellow phase exhibits very sharp, well-defined absorption bands with the lowest energy optical transition occurring at about 510 nm. This is in contrast to the other urethane-substituted poly(diacetylenes), for which it is not possible to isolate an ordered form of the thermally induced second phase at room temperature.

Infrared thermal analysis of HDI-5,7-1000 clearly demonstrated[6] that the thermochromic transition was not the result of an order-disorder transition involving thermal disruption of its interurethane hydrogen bonded network. The complexity of the two-phase nature of this material, however, might suggest that this behavior was unique to this new poly(diacetylene) system. Thus, in order to seek out the generality of this phenomenon and to gain a better understanding of the origin of these unusual color changes, we have extended our studies to include more conventional urethane-substituted poly(diacetylenes) such as poly-ETCD.

Experimental Section

ETCD was prepared according to the procedures described in Sandman et al.[7] Samples for infrared and visible spectroscopy were prepared by casting the monomer from acetone solutions onto potassium bromide windows. The thin-film castings were then thoroughly dried to remove residual solvent and in some cases subsequently polymerized by exposure to UV radiation of 3 mW/cm^2 for 30 min (90% of the output energy is at 254 nm). Samples for DSC studies were prepared by growing crystals of the monomer from ethyl acetate solutions. In this case, polymerization of the monomer was accomplished with a ^{60}Co γ radiation dose of at least 60 Mrads over 4 weeks.

Infrared spectra were recorded on a Nicolet 20 DX Fourier transform infrared spectrophotometer (FTIR). Temperature studies were conducted with a heated precision cell equipped with

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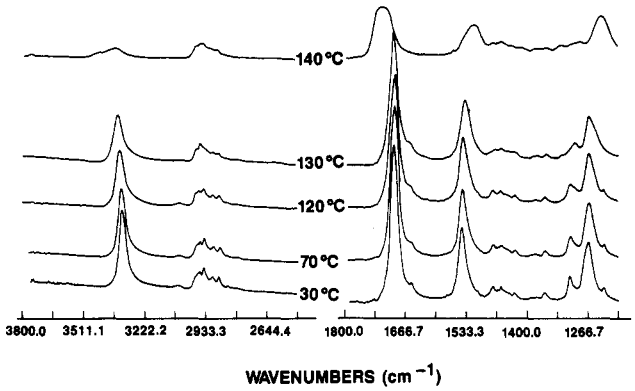

Figure 1. FTIR spectra of ETCD monomer recorded at various temperatures.

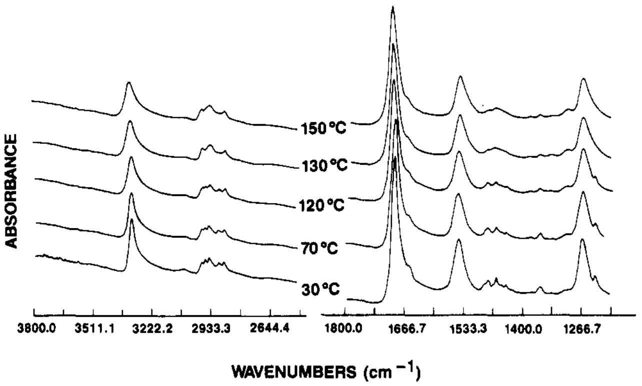

Figure 2. FTIR spectra of poly-ETCD recorded at various temperatures.

a Fenwal Model 550 temperature controller (temperature range from 25 to 200 °C). Peak areas were recorded after the peaks reached a constant value of absorbance (typically after 5 min at a given temperature).

Differential scanning calorimetry (DSC) thermograms were acquired with a Du Pont 1090 thermal analyzer equipped with a DSC module. Samples were run at 10 °C/min under nitrogen using 10–15 mg of sample per run. Transition temperatures were taken as the maxima in the endothermic peaks.

Visible absorption spectra were recorded with a Cary 17D spectrophotometer. Temperature studies were conducted with the same temperature-controllable precision cell described for the infrared studies.

Results

In order to assess the influence of hydrogen bond disruption on the key vibrational modes of poly-ETCD, we first examined the infrared spectrum of ETCD monomer as a function of temperature. This material thus serves as a model compound useful for identifying thermally induced spectral changes in the vibrational bands associated with the proton donor and acceptor of the hydrogen bonds. The two spectral regions of interest are shown in Figure 1. In the N–H stretching region between 3500 and 3100 cm^{-1}, a single, relatively sharp N–H stretching band is observed at about 3324 cm^{-1} at room temperature. The frequency, intensity, and breadth of this band are characteristic of fully hydrogen bonded N–H groups confined within a three-dimensionally ordered monomer matrix.[8] As the temperature is increased to 130 °C, the N–H stretching band decreases slightly in intensity, increases slightly in breadth, and shifts to higher frequencies. These minor changes in the absorption profile can be attributed to an increase in the urethane–urethane contact distance occurring as the monomer matrix undergoes thermal expansion. Between 130 and 140 °C, however, a dramatic broadening and decrease in the intensity of the N–H stretching band occurs and a new higher energy absorption band at frequencies above 3400 cm^{-1}, which can be assigned to free N–H groups, is observed as a shoulder on the original absorption band. This, of course, is the temperature at which the monomer melts and extensive hydrogen bond disordering and dissociation take place.

Similar observations can be made by examining the temperature dependence of the carbonyl absorption band centered at about 1690 cm^{-1}. In this case it can be seen that at temperatures below the melting point of the monomer a relatively temperature-insensitive, sharp absorption band characteristic of hydrogen bonded carbonyl groups in ordered crystalline regions is observed,[8] whereas above the melting point this band shifts abruptly to higher frequencies and becomes extremely broad. In light of the recent publications by Coleman and colleagues,[8] this very broad carbonyl absorption can be attributed to the existence of both non-hydrogen bonded (free) carbonyl groups and highly disordered hydrogen bonded carbonyl groups. Thus, both the N–H and the carbonyl stretching regions display very dramatic and easily discernible spectral changes when a transition from an ordered fully hydrogen bonded state to a highly disordered and partially non-hydrogen bonded state takes place. Having identified the spectral changes characteristic of hydrogen bond disruption in this particular system, we now turn our attention to poly-ETCD.

The FTIR spectra of poly-ETCD recorded as a function of increasing temperature are found in Figure 2. It should first be mentioned that visible absorption spectra of similarly prepared samples recorded as a function of increasing temperature revealed that the thermochromic transition of this poly(diacetylene) takes place between 110 and 130 °C. As can be seen in the figure, no indication of non-hydrogen bonded urethane groups or a significant portion of highly disordered hydrogen bonds can be detected over the entire temperature range of these experiments. Thus, the FTIR spectra clearly show that poly-ETCD is comprised of highly ordered, fully hydrogen bonded urethane groups and, more importantly, that this state of strong urethane–urethane association is retained at temperatures above the thermochromic transition. This can be illustrated graphically by plotting the integrated intensity of the entire N–H stretching region as a function of temperature. Since the intensity of the free N–H stretch is much less than the intensity of the bonded stretch, the total integrated intensity of the N–H absorbance will decrease as the amount of hydrogen bonding within the sample decreases. This parameter has been used extensively[9] as a measure of the extent of hydrogen bonding in polyurethanes and polyamides, and, although it has been recently shown that this simple two-state model can lead to overestimations of the fraction of free N–H groups,[8] it does provide useful information about thermally induced changes in the local environment and order of the hydrogen bonds. In addition, it is well-known that the integrated intensities of certain vibrations are linearly dependent on temperature due to their sensitivity to intermolecular interactions which tend to be reduced as molecules expand with increasing temperature.[10] As a result of this latter phenomenon, transitions involving changes in the thermal coefficient of expansion of a material will give rise to slope discontinuities in these temperature vs. absorbance curves.

The integrated absorbance of the N–H region (normalized to the room-temperature value) as a function of temperature for both ETCD monomer and poly-ETCD are found in Figure 3. For ETCD monomer, there is a rapid decrease in the integrated absorbance of the N–H region

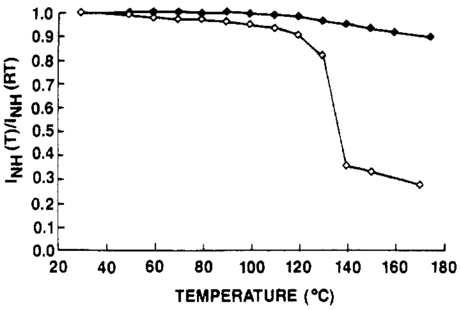

Figure 3. Integrated NH absorbance (normalized to room temperature) as a function of temperature for ETCD monomer (open circles) and poly-ETCD (closed circles).

occurring at about 130 °C due to monomer melting and the concomitant disruption of the hydrogen bonded network. This curve dramatically depicts the major changes in hydrogen bonding that can occur during an order–disorder transition in which ordered regions of hydrogen bonded urethane groups are converted into regions containing both disordered hydrogen bonded urethane groups and free urethane groups. In sharp contrast, it can be seen that the integrated absorbance of the N–H region of poly-ETCD is remarkably constant over the entire temperature range presented in the graph. However, there is a clear slope discontinuity that occurs at the same temperature at which poly-ETCD undergoes its thermochromic transition. Also, around this same temperature, the frequencies of both the carbonyl stretching vibration and the N–H stretching vibration abruptly shift about 3 cm^{-1} to higher energies. Both of these last observations indicate that a sudden expansion of the polymer matrix has occurred, causing a slight change in the local environment of the hydrogen bonded urethane groups during the thermochromic transition.

It is clear from the above discussion that the thermochromic transition of poly-ETCD is not an order–disorder transition driven by the disruption of hydrogen bonds in the side groups as is the case for poly(nBCMU). However, closer inspection of the spectra presented in Figure 2 reveals that, although hydrogen bonding is retained during the thermochromic transition, the vibrational bands associated with the conformational order of the methylene atoms connecting the urethane groups to the conjugated backbone are undergoing major spectral changes at the transition. For example, in the region dominated by methylene symmetric and antisymmetric stretching modes between 2800 and 3000 cm^{-1}, it can be seen that the fine structure attributed to conformationally ordered methylene groups is completely lost above the thermochromic transition. The methylene deformation modes centered around 1450 cm^{-1} also change abruptly above the transition from a collection of sharp, structured absorption bands to a very broad essentially featureless absorption band. All of these changes suggest[11] that the methylene segments of the side groups have undergone a transition from a conformationally ordered state in which the methylene segments are locked into a specific conformational arrangement to a highly disordered state in which all conformational regularity is lost and the methylene groups become fluid, free to adopt many random conformations.

Before proceeding to the discussion of these results, it is worthwhile to briefly describe some of the relevant thermal properties of poly-ETCD. The DSC thermogram of as-prepared poly-ETCD is shown in Figure 4. Three distinct endotherms are observed at 128, 223, and 291 °C. The higher temperature endotherm (291 °C) corresponds, in part, to degradation of the material as indicated by the detection of weight loss in this temperature range by thermogravametric analysis (TGA). The endotherm at 223 °C, on the other hand, can be attributed to a complete melting of the polymer lattice. Of particular interest to this work is the lower temperature endotherm occurring at 128 °C, which takes place at the same temperature as the thermochromic transition of poly-ETCD (110–130 °C). Over this same temperature range, poly-ETCD also undergoes an abrupt macroscopic volume expansion that is readily detected by thermal mechanical analysis (TMA).[12a,13] Both of these thermally induced events are nearly reversible if the sample is not heated much above the transition temperature. The occurrence of both enthalpy and volume discontinuities at this temperature indicates that the thermochromic transition of this material is best defined as a first order phase transition.

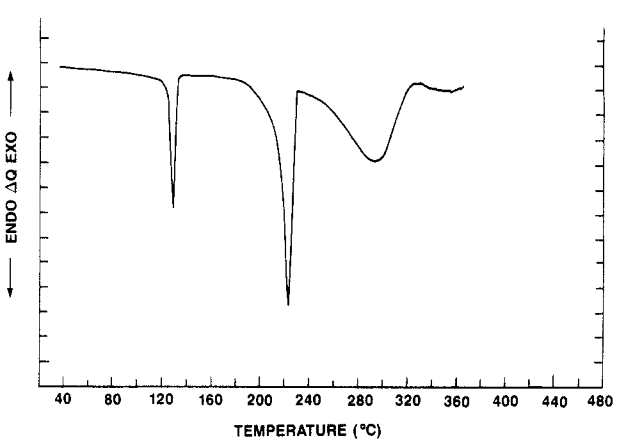

Figure 4. DSC thermogram of poly-ETCD.

Published[4] lattice constants, derived from single-crystal photographs, suggested that the poly-ETCD lattice undergoes a volume contraction between room temperature and the temperature of the thermochromic change. Recently,[14] however, X-ray powder diffraction of poly-ETCD recorded at 20, 100, and 130–135 °C revealed that all major reflections move to larger *d* values at temperatures between 100 and 130–135 °C, indicating that the lattice expands during the transition rather than contracting. Thus, the abrupt macroscopic volume expansion detected during the thermochromic transition of poly-ETCD can be attributed to a microscopic expansion of the poly-ETCD lattice.

Discussion

From the many discussions in the literature about the reversible and irreversible thermochromic transitions of poly(diacetylenes), it is clear that these unusual color changes are related to the sensitivity of the poly(diacetylene) conjugated backbone to changes in the organization and packing of their side groups.[15,16] The side groups impose certain dimensional constraints upon the polymer chain which result in distortions of the backbone primarily in the form of static deformations of bond lengths and/or bond angles. These distortions, in turn, influence the electronic states of the π-electrons of the backbone, presumably via variations in the degree over which the fundamental excitations of the conjugated chain are delocalized over the backbone atoms. Recent theoretical calculations[12,16] have demonstrated that these distortions can indeed give rise to the shifts in optical energies observed during thermochromic transitions. It is to be expected that variations in the inter- and intramolecular interactions of the molecules of the side chains will have a profound effect on the optical properties of these materials. The presence of strong, highly directional nonbonded interactions such as would occur in side groups that hydrogen bond is therefore expected to strongly influence the thermochromic transitions of the poly(diacetylenes).

In the case of poly(nBCMU), the hydrogen bonded network of the side groups is extensively disrupted during the thermochromic transition. This is not too surprising since it is known that hydrogen bond dissociation is controlled by the mobility and rotational freedom of the molecular segments containing the hydrogen bonded groups. For poly(nBCMU), the side groups consist of highly flexible butoxycarbonyl segments which exhibit low energy barriers to rotation and significantly increase the entropy of the molecule upon transition to a liquidlike state. In fact, it is this high degree of side-group flexibility that is responsible for the unusually high solubility of these poly(diacetylenes) in various polar solvents. Thus, any dimensional constraints imposed on the backbone by the packing of the side groups in their ordered hydrogen bonded state are removed at the transition temperature as the side-group atoms "melt" and achieve a highly disordered liquidlike state. As a result of the disorder created in the side groups, the conjugated backbone is now free to adopt a less planar conformation, which dramatically increases the energy of the optical transitions of its valence electrons. The optical manifestations of this process are the shift of the lowest energy optical transition to much higher energies and the complete loss of any structure present in the original absorption band. Similar spectral changes are observed when a thermodynamically "good" solvent is added to a solution of poly(nBCMU) dissolved in a poorer solvent.[1] Thus, the chromic shifts taking place via solvent and/or temperature changes in poly(nBCMU) are due to a related disordering process that ultimately produces a more deformed, less planar polymer backbone.

The high entropy content of the side groups of poly(nBCMU) strongly influences the structural changes that take place during the thermochromic transitions exhibited by this particular class of poly(diacetylenes). For urethane-substituted poly(diacetylenes) that do not contain highly flexible, entropically "active" side groups, however, the molecular rearrangements that take place during the thermochromic transition are quite different. The thermochromic transition of poly-ETCD, for example, occurs without disruption of the hydrogen bonded network and with retention of crystallinity. For this class of poly(diacetylenes), the segmental mobility of the side groups at the transition temperature is not high enough to overcome the rotational barriers needed to achieve a non-hydrogen bonded conformation. Thus, for polymers such as poly-ETCD, poly-IPUDO, and HDI-5,7-1000, the concept of thermochromic transitions facilitated by hydrogen bond disruption in the side groups is not valid, and a new explanation for the origin of thermochromism in these materials is needed.

We propose that at room temperature the conjugated backbone is locked into a more planar conformation by the strongly associated and tightly packed side-group atoms. During the thermochromic transition, the polymer undergoes a volume expansion that occurs with complete retention of hydrogen bonding. As a result of this expansion and the ample energy available for segmental motions, the packing of the side groups becomes less rigid and the methylene segments joining the urethane groups to the backbone are free to explore many different conformations via torsional motions about their side-chain axes. The more fluid nature of the side-group atoms partially relieves the dimensional constraints imposed on the backbone, allowing it to take on a less planar conformation. Since complete disordering of the side groups is prevented by the existence of hydrogen bonding, the side groups still restrict the torsional mobility of the conjugated backbone, thereby preventing it from achieving the highly deformed state characteristic of a poly(diacetylene) chain dissolved in a good solvent. Thus, although the change in backbone planarity gives rise to dramatic optical shifts to higher energies, the absorption bands of the high-temperature phase still retain some structure indicative of the presence of a more ordered poly(diacetylene) environment. The recent theoretical calculations of Orchard and Tripathy[16] clearly show that the changes in backbone planarity allowed within the overall constraints of the hydrogen bonded lattice are sufficient to produce the optical shifts observed during the thermochromic transition.

In some ways, this transition is similar to the reversible pretransitions exhibited by bilayer structures of phospholipids and Langmuir–Blodgett multilayer films of certain fatty acids[11] in which the methylene segments undergo local reorganization and disordering below the melting temperature of the material. The disorder introduced during the pretransition is reversible as long as the hydrophilic portion of the molecule remains "anchored" within the lattice, the similarity being that, in the case of poly-ETCD, the thermochromic transition is reasonably reversible as long as the material is not heated to its melting point after which the transition becomes completely irreversible. Heating poly-ETCD to temperatures below the melting point (223 °C) but much above the transition temperature also negatively influences the reversibility of the transition, causing it to shift to lower temperatures as the material is thermally cycled to increasingly higher temperatures. Thus, as long as the hydrogen bonded urethane groups remain intact within the lattice, the structural changes taking place in the hydrocarbon portion of the side groups are reversible. Heating the polymer to its melting temperature, however, results in the disruption of the hydrogen bonded network and the catastrophic destruction of the lattice.

To summarize, urethane-substituted poly(diacetylenes) containing side groups less entropically "active" than poly(nBCMU) exhibit partially reversible first-order thermochromic transitions that do not involve the loss of hydrogen bonding in the side groups. For these materials, it appears that the observed color changes from blue to red are related to an abrupt volume expansion of the unit cell and the concomitant disruption in the local order and packing of the methylene segments connecting the urethane groups to the backbone. The transition of the methylene segments from a conformationally ordered state to a less rigid disordered state unlocks the conjugated backbone from its planar or near-planar conformation as it is now free to relax due to its greater degree of torsional freedom. Complete relaxation to a highly deformed, nonplanar conformation, however, is prevented by the retention of the three-dimensional order of the polymer lattice and hydrogen bonding within the side groups. This is in contrast to the thermal behavior of poly(nBCMU) and similar poly(diacetylenes) dissolved in thermodynamically "good" solvents in which the elimination of inter- and intramolecular side-group interactions such as would occur with the disruption of hydrogen bonds allows the conjugated backbone to adopt a backbone conformation completely free of side-group constraints.

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Thermodynamics of the Separation of Biomaterials in Two-Phase Aqueous Polymer Systems: Effect of the Phase-Forming Polymers

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ABSTRACT: The liquid lattice theory of Scheutjens and Fleer for the adsorption of polymers from dilute solution to infinite flat surfaces was modified to be applicable to solid particles of arbitrary size and shape with homogeneous surface properties. The model was applied to globular proteins, assumed to be representable as hard spheres, and the Gibbs energy per particle was calculated as a function of the particle size, the polymer chain length, the polymer concentration, the Flory–Huggins interaction parameter, and the segment–surface interaction parameter. Applications of the model to the distribution of proteins between the phases of aqueous two-phase polymer systems and to protein precipitation from solution by the addition of poly(ethylene glycol) yielded results in good agreement with experimental data.

Introduction

Recent advances in the fields of medical technology and biochemistry have focused interest on understanding the nature of interactions between biological macromolecules and other natural and synthetic polymers. Such an understanding is critical to applications ranging from the development of biocompatible materials for artificial organs to the use of polymers as flocculating or stabilizing agents in biopolymer solutions. One particular area of interest to the biochemicals industry is the use of water-soluble polymers to separate colloidal bioparticle mixtures by using so-called "two-phase aqueous polymer systems".

It has long been known[1-4] that, in general, solutions containing two different polymers are immiscible and resist formation of a single phase even when the system is diluted with considerable amounts of a solvent that is completely miscible with the pure polymers. This behavior has been explained in the framework of polymer solution theory,[5-7] and many examples of three-component systems (polymer X/polymer Y/solvent) containing large two-phase regions in the phase diagram are presently known.[1-4]

In the late 1950s, Albertsson[1] discovered in his work with aqueous two-phase polymer systems that low concentrations of a fourth component, i.e., a third solute, added to such systems distributed unevenly between the two phases, so long as this new component was relatively "large" (solutes with dimensions roughly in the range 30 Å [proteins] to 10 μm [whole cells] were investigated). Albertsson exploited the preference of particles for one of the two phases successfully in designing a countercurrent extraction process for the separation and purification of biological macromolecules and colloidal systems.[1,8-10] Since then, extensive experimental research on these liquid–liquid extraction systems has been conducted in many laboratories (see ref 1, 11, and 12 for a literature review) and large-scale separation processes have been developed.[1,13,14] The technique has many practical advantages: the process may be operated continuously in a countercurrent configuration and is easily scaled up.[13] Perhaps most significantly, however, the technique provides a gentle, protective environment for the biological material since both phases in the biphasic system are comprised primarily of water. (Enzymes, for instance, typically retain a large fraction of their activity during such separations.[1,13])

Despite the success of aqueous two-phase polymer systems for biomaterial separation, the factors and mechanisms that bring about the uneven distribution of particles between the two phases are not understood. Some heuristic rules exist,[1,12] but no comprehensive theory has been developed to help guide the design of systems for the separation of specific mixtures. As a result, application of the technique requires tedious hit-or-miss experimentation.[13]

Here, we develop a model of the basic interactions and mechanisms acting in the distribution of particulates between two polymer solution phases. The model provides a detailed description of the particle in aqueous polymer solution but does not include the effects of salts and pH.

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