Stoichiometrically Solvated Polyalkylbenzimidazole Crystals

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Synopsis

Unlike most crystallizable polymers, some polyalkylbenzimidazoles do not crystallize when pure but do crystallize with ionized solvent molecules to produce solid stoichiometrical, solvated crystals. The polymer–solvent interaction is strongly exothermic, and a crosslinked polymer swells in the solvent over hundredfold. This leads to a negative χ_1 value for the system. The cocrystallization with stoichiometric amounts of ionized solvent cannot be examined on the assumption that it is a polyelectrolyte gel since ion mobility is precluded. It also cannot be treated according to the corresponding states theory since the latter does not allow for negative χ_1. A theoretical derivation, originating from Flory's semiflexible chain treatment, apparently predicts and explains the behavior of the polyalkylbenzimidazole–solvent system.

INTRODUCTION

Most crystallizable high molecular weight polymers are characterized by relatively flexible chains. The behavior of such polymers in solution, or in the solid but in the presence of a solvent, was successfully described by the Flory-Huggins[1,2] lattice theory and by the Patterson-Delmas[3,4] and Flory and coworkers[5,6] theories of the corresponding states. When crystallized out of solution, or from the amorphous solid in the presence of some solvent, the polymer crystals are comprised solely of polymeric macromolecules. X-Ray diffraction patterns indicate that the crystalline bulk is essentially the same for the melt- or solvent-crystallized polymer.

A group of other polymers, with rather rigid chains and an ability for strong interactions with certain solvents, form liquid crystals when they are in sufficiently concentrated solutions. The onset of ordering due to formation of liquid crystals is accompanied by a sharp drop in the viscosity of the solution as it reaches a characteristic concentration. This was observed, for example, in poly(γ-benzyl-L-glutamate) in m-cresol[7] and poly(p-benzamide) in N,N'-dimethylacetamide–LiCl solutions.[8,9] The performance of such polymers in solvent, as a solution or a two-phase system, was predicted with remarkable accuracy[10] by Flory in his treatment of semiflexible[11] and rod-like[12] chain molecules.

Several other crystallizable polymers crystallize in one form in the absence of a complexing agent and cocrystallize in a different form with a complexing agent. Among these, one finds the nylon 6–iodine complex yielding the crystalline γ form,[13,14] the polyacrylonitrile–iodine crystalline complex,[15] the coiled amylose V complexes with various alcohols,[16,17] and the monohydrate of po-

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ly(oxacyclobutane)[18,19] where the polyether chains are arranged each in a planar zigzag to form hydrogen-bonded planar ribbon-like structures.

One additional group of polymers exists which does not fit in any of the above categories. This group includes at least two symmetric and one nonsymmetric polyalkylbenzimidazoles, and possibly a fully aromatic polybenzimidazole and poly(amide-benzimidazole). When pure, these polymers are amorphous and do not crystallize from the melt. When crystallized out of solution, or in the solid state in the presence of an appropriate solvent, they incorporate in the crystal lattice stoichiometric amounts of solvent of crystallization. The two symmetric aliphatic polymers showing this behavior are poly(2,2'-octamethylenebisbenzimidazole) (POMBBI)[20] and poly(2,2'-octamethylene-5,5'-dibenzimidazole) (POMDBI).[21-23] The solvents with which these polymers cocrystallize are formic acid[20,22] and trifluoroacetic acid.[24] The unsolvated polymers are hygroscopic[24] and when precipitated from water tend to form a hemihydrate.[25] The fully aromatic polybenzimidazole yields crystalline diffraction patterns after treatment with phenol and water under high pressure and temperature.[26] From the given data, one cannot conclude whether this polymer crystallizes by itself and the phenol–water serves only as plasticizing agents or whether the polymer cocrystallizes with either or both of the micromolecular species. An aromatic poly-(amide-benzimidazole) forms a dihydrate,[27] but the level of order as detected by x-ray techniques is marginal, making the crystallinity of this dihydrate doubtful.

The thermodynamic treatment of Frenkel and associates[9,23,28] of the crystallization of POMDBI in the presence of formic acid failed to take cognizance of the stoichiometric relation and the chemical reaction between polymer and solvating molecules. As will be presently shown, precisely these two facts control the cocrystallization of symmetric polyalkylbenzimidazoles with solvents of crystallization.

EXPERIMENTAL

The symmetric poly(2,2'-octamethylenebisbenzimidazole) (POMBBI)[20] and poly(2,2'-octamethylene-5,5'-dibenzimidazole) (POMDBI)[24] were prepared in poly(phosphoric acid) by condensation of sebacic acid with 1,2,4,5-tetraamino-benzene·4HCl and 3,3'-diaminobenzidine, respectively. The procedure was essentially that of Iwakura et al.[25]

The nonsymmetric poly(2,5-trimethylenebenzimidazole) (PTMBI) was prepared[20,29] by melt polymerization of its diamine monoester monomer. Poly(2,5-ethylenebenzimidazole) (PEBI), another nonsymmetric polyalkylbenzimidazole, was kindly supplied by Mrs. E. A. Turi of Allied Chemical Corporation. The polymer was melt polymerized as described by Shalaby and associates.[30]

Infrared scans were obtained from thin films of the solvated polymers or KBr pellets containing some pulverized pure or solvated-crosslinked polymer. X-Ray diffraction patterns were obtained photographically for POMBBI and PTMBI[20] and diffractometrically for POMDBI and PEBI.[24] In all instances, the solvated and pure polymers were dried in vacuum ovens at temperatures from 110°C to 135°C prior to the scans. The polymers were deemed sufficiently dry when they reached constant weight and when infrared scans showed no bands associated with the presence of water or free solvent. The two nonsymmetric polyalkyl-

benzimidazoles were tested for crystallinity in the pure and solvated forms and also as their HCl adducts.

Separation between crosslinked and uncrosslinked polymer was done on the basis of dissolution in boiling formic acid, the crosslinked polymer being obtained from the uncrosslinked one by heating at temperatures above 215°C. Solvation of the uncrosslinked and swelling of the crosslinked polymer were obtained in sealed containers by two means: (1) placement of the polymer in a large amount of solvent and removal of the excess solvent after the polymer dissolved or swelled, or (2) exposure of the carefully dried polymer solely to the vapors of the solvent. Both techniques yielded the same results.

RESULTS

The intrinsic viscosities in formic acid of the polybenzimidazoles prepared in the course of this work were 5.85 for POMBBI,[20] 1.75 for POMDBI,[24] and 1.46 for PTMBI.[20] These polymers and PEBI are highly soluble in formic acid. They are also soluble in trifluoroacetic acid and, to a lesser degree, in dimethyl sulfoxide and N,N'-dimethylformamide. PTMBI tends to form a 1:1 hydrochloride adduct which, in turn, is highly soluble in dilute HCl.

Gravimetric and elemental analyses of the dry polymer–solvent systems indicated that the polymers form stoichiometric adducts with the solvents. POMBBI forms a 1:2 complex with formic acid (two formic acid molecules per repeat unit).[20] POMDBI also complexes with acids. At constant weights, the amounts of adduct acid per gram of polymer are 0.265 g of formic acid and 0.665 g of trifluoroacetic acid, indicating 1:2 polymer–acid adducts.[24] PTMBI forms a 1:1 adduct with HCl and with formic acid.[20,29]

The density of the POMDBI pure polymer was determined in a dichloromethane/heptane mixture to be 1.095 ± 0.005 g/cm^3. The solvated-crystalline POMDBI·2HCOOH yielded a density of 1.305 ± 0.005 g/cm^3 in a carbon tetrachloride/heptane mixture. The density of formic acid is 1.22 g/cm^3. It is obvious that the density of the solvated crystals is far higher than that expected from simple additivity. The difference between the pure and the solvated polymer is 0.210 g/cm^3, rather close to the weight of formic acid taken up by a gram of polymer upon solvation. Based on the above, one may hypothesize that the formic acid molecules enter the solvating polymer and cocrystallize in it with only a very small increase in the average distance between the polymeric chains.

When the crosslinked POMDBI was immersed in formic acid, it underwent extensive swelling. After reaching equilibrium, the excess formic acid was filtered away and the swollen material dried gently with a filter paper and weighed. From the measured weight and specific density of formic acid, it was determined that the ratio of the swollen to unswollen polymer, q_m, was 108.2. Volumetric measurements also yielded about the same value for q_m. In water, the material deswelled to a q_m of only 30. When the uncrosslinked POMDBI is subjected to the same treatment, it goes into solution with an initial increase in volume of no more than 25%. Fixed amounts of POMDBI and formic acid in separate containers equipped with thermometers were allowed to equilibrate at room temperature. Then the POMDBI was poured into the formic acid with light stirring. In both instances, crosslinked and uncrosslinked polymer, there occurred a fast increase in the temperature of the system, reaching a maximum

TABLE I
Diffraction Patterns of Crystalline Polyalkylbenzimidazole Adducts

Intensity	d, Å		
	POMBBI·2HCOOH[20]	POMDBI·2HCOOH[24]	POMDBI·2CF₃COOH[24]
s	15.35	8.04	9.41
sb	11.53	5.31	4.65
w	8.03	4.31	4.06
s	7.17	4.00	3.45
w	5.33	3.59	
m	4.43		
w	4.28		
s	4.05		
s	3.84		
m	3.33		
vvw	2.90		
vvw	2.10		

within about 1 min. The exothermic changes in temperature were calculated to be 1.25°C/g of crosslinked polymer and 2.22°C/g of uncrosslinked polymer.

Infrared spectra of the dry stoichiometric polymer–solvent adducts revealed that no free acid was present in such systems. Scans of POMBBI·2HCOOH adducts contained absorption bands at 1580 and 1330 cm^{-1} associated with the formate ion.[31] The band at about 1700 cm^{-1}, associated with the free carboxylic acid, was completely absent.[20] In the case of POMDBI·2HCOOH, the presence of absorption bands at 1530 and 1340 cm^{-1} and their absence at about 1700 cm^{-1} indicate that the polymer is complexed with formate ions and not with formic acid.[24,31] In the case of POMDBI·2CF₃COOH, two very intense bands at 1670 and 1200 cm^{-1}, associated with the trifluoroacetate ion, are present in the infrared spectrum, while the band at 1825 cm^{-1}, associated with the free trifluoroacetic acid,[32] is completely absent.

The infrared spectra of crosslinked POMDBI dried to constant weight from its swollen state in formic acid contains bands at 1340, 1530, and 1690 cm^{-1}, indicating the presence of both the formate ion and the free formic acid.

In the pure, dry, and unsolvated polymers the above bands are missing, of course. A band at 3400 cm^{-1} becomes prominent, however. Upon solvation, the band disappears. Since this band is characteristic of free NH groups,[23] it is obvious that upon solvation, free NH groups cease to exist. The disappearance of the free NH of benzimidazole residues and the presence of only carboxylate ions in the stoichiometric adducts indicate that each bound acid molecule donated one proton to each imidazole ring, creating chains of carboxylate ions each bound to two imidazole rings in two different benzimidazole residues. One of these bonds is ionic, and the other is a hydrogen bond.

Some of the polyalkylbenzimidazole–carboxylate or the polyalkylbenzimidazole–hydrochloride stoichiometric adducts were crystalline while others remained amorphous. The x-ray diffraction patterns of the more crystalline adducts are given in Table I. The amount and level of crystallinity of the POMDBI adducts are markedly lower than those of the POMBBI adduct. The adduct of PTMBI hydrochloride with formic acid yielded a few crystalline reflections of very poor resolution, indicating only a very low degree of perfection

and a minor amount of crystallinity in the sample. When the PTMBI was neutralized and the neutral polymer cast from formic acid solution, no crystallinity at all was detected. Attempts to induce crystallization in PEBI failed. The polymer alone, or its hydrochloride adduct, cast from formic acid or from trifluoroacetic acid, generated not even a hint of a crystalline reflection in the x-ray scans. The nonsolvated uncrosslinked POMDBI, the POMBBI, PTMBI·HCl, PTMBI, and PEBI, and the crosslinked polymers were all amorphous according to their x-ray patterns.

The x-ray patterns of drawn and undrawn films of the adduct POMBBI·2HCOOH showed a number of reflections sufficient for the calculation of the adduct's unit cell. This was tentatively determined to contain eight polymeric repeat units with their formate ions and to be orthorhombic with $a = 16.22$ Å, $b = 15.36$ Å, and $c = 17.35$ Å.[20]

It is most probable that the stoichiometrically solvated polymeric chains exist in the crystallites in the trans conformation. This is brought about by the mutual repulsion of the ionic species, the carboxylate ions and imidazolium rings, maximizing the distance between ions of the same charge, and by doing so uncoiling and extending the chains. This is essentially an ionomeric mutual repulsion behavior as was shown, for example, by Katchalsky et al.[33] for ionized poly(methacrylic acid).

The above results indicate that the pure, dry, and uncrosslinked polyalkylbenzimidazoles are amorphous. In contact with such solvents as formic, trifluoroacetic, or hydrochloric acids, stoichiometric adducts can form. In these stoichiometric adducts, the solvating acids and the polymers are in their ionized form. The per cent crystallinity and its perfection decrease in the order POMBBI·2HCOOH > POMDBI·2HCOOH > POMDBI·2CF$_3$COOH > PTMBI hydrochloride formate. PTMBI·HCl, PTMBI·HCOOH, and all PEBI adducts are amorphous, and so are the solvated and unsolvated crosslinked polymers. The polymer chains in the crystalline POMBBI·2HCOOH and POMDBI adducts are probably in the trans conformation in one direction, while ionic and hydrogen bonds between polymer chains and solvate ions form chains along an essentially perpendicular direction. The process of dissolution of POMDBI in formic acid is strongly exothermic. When crosslinked, it swells in formic acid over a hundredfold in a highly exothermic fashion.

DISCUSSION

The results show that some polyalkylbenzimidazoles are amorphous when completely dry. In the presence of certain ionizable solvents, stoichiometric solvates are formed. Several of these are crystalline. The crystalline stoichiometric solvates have three common characteristics: (1) Ionic and hydrogen bonds form between the polymer repeat units and the ionized solvent molecules present in the crystal lattice in well-defined stoichiometric quantities. (2) Each bound carboxylate ion forms two bonds with two different polymer repeat units. (3) The polymeric chains are in essentially a fully trans conformation, probably due to electrostatic repulsion between the ionic species in the stoichiometric adducts.

The Flory-Huggins theory cannot explain such a behavior because of several reasons. Prominent among them are: (1) The theory treats only nonpolar or

weakly polar solvent–polymer pairs. (2) The theory is not meant to treat ionized and unionized species of the same constituents coexisting in the same system in one or more phases. (3) The theory assumes that each solvent molecule and polymer segment occupy one lattice site and that all such sites are equal in size. It is highly unlikely that in the solvated stoichiometric crystals, with the chains mostly in trans conformation, the lattice sites will have the same size as in the solution.

Other approaches, such as the application of partition functions at the thermodynamic limit,[34] where energy fluctuations become important, may conceivably be used to describe the system. Since there are four different species in our systems, some difficulties in the employment of such techniques may, however, arise.

In this paper we chose, therefore, to start from the system of semiflexible chains and micromolecular solvent described by Flory.[11] This is also because the system encountered by us bears some similarity to the system described by Flory. His treatment dealt with the case of randomizing in a single solution the two phases of pure solvent and fully ordered semirigid polymer. Our situation involves the combination of two random phases of solvent and amorphous polymer to form an ordered single-phase stoichiometric adduct in which the polymer chains are essentially in trans conformation, behaving in a semiflexible manner. Some important differences between the two systems will become obvious in the course of the following discussion.

Let us start, then, with the definition of the free energy of mixing pure solvent and an ordered polymer:[11]

$$\Delta G_M = \Delta G_M^* + \Delta G_d \qquad (1)$$

where

$$\Delta G_M^* = RT[n_1 \ln v_1 + n_2 \ln v_2 + \chi_1 x n_2 v_1] \qquad (2)$$

is the free energy of mixing chain molecules without altering their configurations in the process; v and n are volume fraction and number of moles, respectively; x is the average number of segments per macromolecule; χ_1 is the interaction parameter between polymer and solvent; and the subscripts 1 and 2 stand, respectively, for solvent and polymer. ΔG_d is the free energy change involved in converting perfectly ordered polymer molecules to a state of random disorder. The reverse process, that of converting polymer molecules from disorder to order, is then $-\Delta G_d$. Taking a page from Flory, we write the free energy of mixing as

$$\Delta G_M = RT\{n_1 \ln v_1 + n_2 \ln v_2 + \chi_1 x n_2 v_1 + n_2 \ln (\tfrac{1}{2}xz) - n_2(x - 1)$$
$$- n_2(x - 2)[f \ln f + (1 - f) \ln (1 - f) - f \ln (z - 2) + f\epsilon/kT]\} \qquad (3)$$

with z being the lattice coordination number, f the degree of chain bending, ϵ a difference in the configurational energy between an available lattice site and all other available lattice sites, k the Boltzmann constant, R the gas constant, and T the absolute temperature. Equation (3) is correct for the case where the polymer molecules become fully ordered in the solution, i.e., semirigid molecules ordered throughout the volume of the solution, when there are no differences in interaction between solvent molecules that are ionized and bound to the polymer and unionized, unattached, solvent molecules.

To describe the systems we are dealing with, one must, hence, account for part of the solvent and polymer forming an ordered solvated crystal structure, and the rest of the solvent and polymer remaining randomized in solution with a different interaction parameter between them. For the purpose of partitioning, it is advisable to redefine z as the number of nearest-neighbor lattice sites available for a solvent molecule around each imidazole ring. When only van der Waals forces operate, $6 < z < 12$, averaging about $z = 9.7$ for micromolecules or segments that can be simulated by hard spheres.[35] When ionic or hydrogen bonds form, $z = 2$. Taking cognizance of the fact that within each phase, the solvated crystal and the solution, all the z positions are equal, one can set $\epsilon = 0$. Inserting this in eq. (3), taking its derivative $\partial \Delta G_M / \partial f$, and equating it to zero, the equilibrium degree of chain flexibility is obtained:

$$f = (z - 2)/[1 + (z - 2)] \tag{4}$$

It is obvious that in the case of the solvating carboxylate form, where the two z sites are equal ($\epsilon = 0$) and the electrostatic charge repulses like ions, the chain will be stretched out as a rod, with $f = 0$. A minor amount of chain flexibility is most probable, however, so that $f \rightarrow 0$. When there exist more z sites, and when free acid and carboxylate ions can freely interchange, transient polymer–solvent bonds form; the polymer chains bend and rotate to accommodate these bonds; and even though on the average $\epsilon = 0$, the chain maintains a measure of flexibility with $0 < f < 1$. This situation exists in polyelectrolyte gels.

Accounting for the partition of solvent and polymer between the two phases, for the fact that $\epsilon = 0$, and for the solvent being neutral in solution and ionic in the stoichiometric crystalline solvates, eq. (3) can be redefined as

$$\begin{aligned}
\Delta G_M = RT\{ & n_{1s} \ln v_{1s} + n_{2s} \ln v_{2s} + \chi_{1s} x n_{2s} v_{1s} + n_{2s} \ln (\tfrac{1}{2} x z_s) \\
& - n_{2s}(x - 1) - n_{2s}(x - 2)[f_s \ln f_s + (1 - f_s) \ln (1 - f_s) - f_s \ln (z_s - 2)] \\
& + n_{1c} \ln v_{1c} + n_{2c} \ln v_{2c} + \chi_{1c} x n_{2c} v_{1c} + n_{2c} \ln (\tfrac{1}{2} x z_c) - n_{2c}(x - 1) \\
& - n_{2c}(x - 2)[f_c \ln f_c + (1 - f_c) \ln (1 - f_c) - f_c \ln (z_c - 2)]\}
\end{aligned} \tag{5}$$

where the subscripts s and c stand for solution and crystal with

$$n_{1s} + n_{1c} = n_1 \tag{6}$$

$$n_{2s} + n_{2c} = n_2 \tag{7}$$

$$v_{1s} + v_{1c} = v_1 \tag{8}$$

$$v_{2s} + v_{2c} = v_2 \tag{9}$$

$$z_s \gg z_c = 2 \tag{10}$$

$$1 > f_s \gg f_c \rightarrow 0 \tag{11}$$

and

$$0 > \chi_{1s} \neq \chi_{1c} \tag{12}$$

The negative value of χ_{1s} arises from the exothermic dissolution of the polyalkylbenzimidazole in the solvent (say, POMDBI in formic acid) and of the extreme swelling of the crosslinked polymer in the same solvent. The inequality $\chi_{1s} \neq \chi_{1c}$ is due to the difference in activity between the neutral and the ionized species; χ_{1s} is, however, conceivably close to χ_{1c}.

In the calculations of χ_{1s} the equation[36]

$$q_m{}^{5/3} = (V_0/\nu_e)(\tfrac{1}{2} - \chi_{1s})/V_1 \qquad (13)$$

was used, where V_0 is the volume of the unswollen polymer, V_1 the molar volume of the solvent, q_m the volume ratio of the swollen to unswollen networks, and ν_e the number of effective chains in the network. Because of the careful extraction of solubles from the crosslinked polymer, the number of effective chains ν_e was estimated to be 90% of the total number of chains in the system, ν:

$$\nu_e \simeq 0.9\nu = V_0/\bar{\nu}M_c \qquad (14)$$

with $\bar{\nu}$ being the specific volume of the unswollen polymer (0.9 cm^3/g in the case of POMDBI) and M_c the molecular weight between crosslinks. An assumption of 1% crosslinked monomer yields $M_c \simeq 34,500$ and 2% crosslinking $M_c \simeq 17,000$. Using the value of $q_m = 108.2$ obtained for POMDBI in formic acid, and inserting several values for the crosslinks density, one obtains from eqs. (13) and (14) an M_c in the order of 250,000 to correspond to $\chi_{1s} = 0$. Smaller M_c values correspond to negative χ_{1s}, with $\chi_{1s} = -2.95$ for 1% crosslinking and $\chi_{1s} = -6.4$ at 2% crosslinks. As the intrinsic viscosity of the uncrosslinked polymer was only 1.75, the value of $M_c \sim 250,000$ seems to be larger than the molecular weight of the uncrosslinked polymer itself, leading us to the inescapable conclusion that for the Flory-Huggins theory to hold, χ_{1s} must have a negative value. Due to the immobility of the solvated ions in the stoichiometric crystal, a treatment of the system as if it were a polyelectrolyte gel is not justifiable.

Negative χ_1 values appear from time to time in the literature.[37–41] They are all characteristic of strongly interacting, highly compatible solvent–polymer pairs. From highly swollen, lightly crosslinked poly(methacrylic acid) gel data given by Katchalsky et al.,[42,43] a value of χ_1 in the order of -40 was calculated by this author. In the Patterson-Delmas theory of corresponding states,[4,44] all the terms in the equation describing χ_1 are nonnegative, leading to $\chi_1 \geqslant 0$. It is obvious that such a theory was not meant to treat highly interacting pairs where χ_1 may be negative.

With a z value of about 9.7 in the solution, $f = 0.885$. Insertion of these values in the square-bracketed term in eq. (5) yields a value of -2.163 for the solution term. In the solvated crystal, with $z = 2$ and $f \cong 0$, the value of the square-bracketed term is zero. Since both terms are multiplied by $-n_2(x - 2)$, which is negative, the last of the solution terms is positive and relatively large, while the last of the solvated crystal terms is zero. The terms $n_2 \ln (\tfrac{1}{2}xz)$ are positive and significantly larger for the solution than for the crystalline phase. The χ_1-containing terms are negative for the solution and possibly negative for the crystal, conceivably of close magnitude. The other terms are all negative. All in all, if the Flory-Huggins theory holds for our systems, then ΔG_M for the solution is more positive and significantly larger than ΔG_M for the solvated crystal. Therefore, when amorphous, completely dried polyalkylbenzimidazole of the type described above is mixed with ionizable solvent sufficient for stoichiometry, solvated stoichiometric crystals form. Upon addition of excess solvent, the solvated crystals dissolve, yielding a homogeneous solution.

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