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containing 70% poly(pivalolactone), all show a surface richer in poly(dimethylsiloxane). Annealing of the polymer samples should cause poly(pivalolactone) to better crystallize and cause more poly(dimethylsiloxane) to appear at the surface.

In conclusion, the chemistry that is described herein offers a new synthetic route to semicrystalline, high molecular weight poly(siloxane)–poly(ester) copolymers. These copolymers are very well phase separated and can be synthesized in a variety of compositions. All compositions exhibit a high melting point, yet offer the surface characteristics of siloxane copolymers. When the composition is rich in the siloxane phase, the copolymer is elastic in its behavior; when the composition is rich in the poly(ester) phase, the copolymer exhibits the properties of an engineering copolymer.

Our future work involves determining mechanical and rheological properties of these materials and expanding the synthesis to fluorinated siloxane copolymers.

Acknowledgment. We thank the Army Research Office for their financial support of this work (Contract DAAL 03-86-K-0050).

Registry No. 18-Crown-6, 17455-13-9.

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Hydrogen Bonding in Poly(amic acid)s

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Received April 22, 1988; Revised Manuscript Received March 14, 1989

ABSTRACT: Hydrogen bonding interactions in the poly(amic acid) precursors to polyimides are thought to significantly affect the curing process. Association models are applied to a calculation of the equilibrium distribution of hydrogen-bonded species. In the absence of a strongly hydrogen-bonding solvent, the principal types of interaction are between functional groups of the same type, i.e., acid/acid, amide/amide. These conclusions are supported by the infrared spectra of solvent-free amic acid and poly(amic acid) films.

Introduction

Numerous studies of the curing of polyimide precursors can be found in the literature. In much of this work the principal tool used to characterize the mechanism and the kinetics of the curing process has been infrared spectroscopy. The functional groups involved in the curing process, carboxylic acids and amides, have strong, easily identified absorption modes near 1700 and 1640 cm^{-1} and the technique is well-suited to the study of films. Upon curing, characteristic imide carbonyl stretching modes near 1780 and 1730 cm^{-1} appear, with the latter being far more intense than the former. (The vibrational character of these modes has been discussed by Matsuo[1] and Vanclef and Bouche.[2]) In many curing studies, however, only the weak 1780-cm^{-1} band is clearly resolved, very thin films being required to prevent "overabsorption" of the more intense mode near 1730 cm^{-1}. As a result, we believe some important information concerning competing reactions that can occur during curing has been lost. This forms the subject matter of these two papers. In this first paper we wish to consider what may at first seem to be a digression from the principal lines of our work: a consideration of hydrogen bonding in the poly(amic acid) precursors.

A number of authors have considered the hydrogen bonding of poly(amic acid)s to various solvents[3–9] and

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0024-9297/89/2222-4159$01.50/0

conclude that the nature of hydrogen bonding in these materials, the pattern of self-association, and the nature of the complex formed with particular solvents have a profound affect on the imidazation mechanism. For example, Ardashnikov et al.[9] assumed the existence of three types of intramolecular hydrogen bonds between ortho carboxy amides and suggested that one of these creates a particularly favorable structure for subsequent cyclization. In our view these proposed hydrogen-bonded structures are unlikely. They consist of seven-membered rings that are inconsistent with the specific, stringent spatial requirements for the formation of such intramolecular hydrogen bonds discussed by Pimentel and McClellan.[10] Recently, Brekner and Feger[7,8] argued that there are two distinct steps in the loss of 1-methyl-2-pyrrolidinone, NMP, from a complex of poly(amic acid) with this solvent and concluded that in the solid state the presence of strong intermolecular hydrogen bonds hinders the conformations that favor imidization and decreases the selectivity of the reactions. This supports the observations of Kreuz et al.[11] and Kardash et al.[12] concerning the favorable effect of residual solvent on chain mobility and hence imidization. Because the work of Brekner and Feger[7] shows that at least in model compounds most of the solvent is driven off prior to the onset of imidzation, the pattern of hydrogen bonding in the nonsolvated amic acid precursor could significantly affect the imidization process. This has not been explored in detail in previous publication and forms the subject matter of this initial paper. Our study is both experimental and theoretical. We will initially demonstrate the use of association models for elucidating the types of hydrogen-bonded structures present; then we compare the theoretical predictions to the results of FTIR measurements.

Experimental Section

The poly(amic acid) used in this study is a poly(pyromellitic dianhydride oxydianiline) obtained as a concentrated solution in NMP (*N*-methylpyrrolidinone) from Du Pont. Films thin enough for transmission IR (a few micrometers) were prepared by casting onto KBr windows; the bulk of the solvent was then allowed to evaporate over a period of several hours at room temperature, and the resulting films were considered "dry" (but *not* solvent free). Thin films of solvent-free poly(amic acid) were prepared by smearing solution onto a glass slide and immediately immersing in distilled water; the free-standing film was then washed repeatedly in fresh water and dried at low temperatures under vacuum. A model amic acid was produced by reacting pyromellitic dianhydride (PMDA) and *p*-anisidine in NMP. Spectra were recorded on a Digilab FTS-60 spectrometer at a resolution of 2 cm^{-1}.

Theory

Our aim here is to develop a description of the type and distribution of hydrogen-bonded species present in poly(amic acid)s and in poly(amic acid)/solvent complexes. We will use an association model that has proved to be very successful in treating hydrogen-bonding interactions in alcohol/hydrocarbon mixtures[13-16] and that we have adapted to the description of hydrogen bonding in polymer blends.[17-22] In this approach, the various hydrogen-bonded complexes are treated as distinguishable species and equations for the stoichiometry of hydrogen bonding and the free energy of mixing are obtained in terms of equilibrium constants that describe the distribution of species present. A major advantage of this model is that these equilibrium constants can, in principle, be obtained from infrared spectroscopic measurements. In this paper we are not concerned with the thermodynamics of poly(amic acid) solutions but the somewhat simpler task of describing the stoichiometry of hydrogen bonding.

Even in a simple poly(amic acid), where the only groups that hydrogen bond are carboxylic acid and amide functionalities, there are still a surprising number of types of hydrogen bonds that can be formed, so that the algebraic form of the equations appears complicated. Nevertheless, the underlying principle is simple; with a prior knowledge of the constants describing the competitive equilibrium between the various species, the system can be defined quantitatively. For this particular problem the errors and limitations of the theory will arise from the use of values of the equilibrium constants determined for systems where the functional groups are not confined to the same repeat unit; in other words, where the functional groups are free to move around at random and find partners according to the statistics of the equilibrium process. For now, we will treat the equilibria between the various types of complexes under the assumption that the constraints imposed by the polymeric nature of the molecules are negligible (essentially, we assume that there is sufficient local flexibility of the functional groups that hydrogen bonds can form according to their intrinsic proclivities).

Association between Carboxylic Acid and Amide Groups. We commence with a simple description of the type of hydrogen-bonded species present and definitions of the equilibrium constants used to describe their association. First, we can have self-association between the amide groups to form chains of hydrogen bonds. Following a convention we employed previously,[17,18] we use the symbol B to represent such units and we assume that the equilibrium constant K_B is independent of the length of the hydrogen-bonded chains that are formed; i.e.

$$B_n + B_1 \underset{}{\overset{K_B}{\rightleftharpoons}} B_{n+1} \qquad (1)$$

where K_B is independent of n. Following Flory,[23] we note that the statistical mechanics of this system requires that the equilibrium constant be defined in terms of molar concentrations or volume fractions rather than mole fractions (a definition of the equilibrium constant in terms of the latter parameters would not account for the difference in size or number of lattice sites occupied by the various polymer species in equilibrium). The correct definition of K_B is then

$$K_B = \frac{\phi_{B_{n+1}}}{\phi_{B_n}\phi_{B_1}} \frac{n}{(n+1)} \qquad (2)$$

Similarly, self-association between carboxylic acid groups (A) to form the characteristic hydrogen-bonded dimers is described by the equilibrium

$$A_1 + A_1 \overset{K_A}{\rightleftharpoons} A_2 \qquad (3)$$

where

$$K_A = \frac{\phi_{A_2}}{\phi_{A_1}^2} \frac{1}{2} \qquad (4)$$

So far, we have left undefined the precise nature of the "monomers" or non-hydrogen-bonded species B_1, A_1, etc. By use of a lattice model to derive these equilibrium constants, it can be shown that the lattice cell size is defined by molar volume of the "true" interacting species, so that ϕ_{B_1} would be the total volume fraction of non-hydrogen-bonded amide "interacting units", and so on.[18] These are not easily defined or readily measured entities. For example, is the interacting unit of the amide group the entire CONH functionality, some fraction of this, or perhaps some larger entity incorporating elements of adjacent

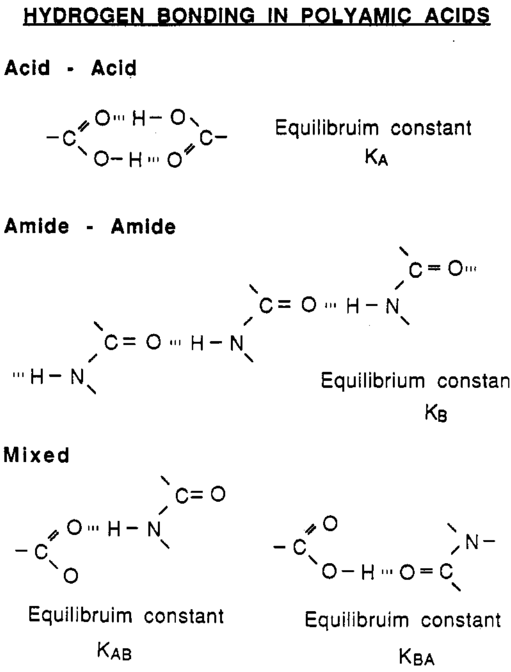


Figure 1. Illustration of the types of hydrogen-bonding interactions that can occur in poly(amic acid)s.

atoms? Fortunately, this is immaterial. We can define the equilibrium constant in terms of the volume fractions of the chemical repeat units in question. This follows directly by letting the self-associating interaction unit in question define the size of a segment (or unit on a lattice), such that

$$S_B = V_{B_1}/V_{\beta 1} \tag{5}$$

where V_{B_1} is the volume of the molecule or chemical repeat unit (for a poly(amic acid)) and $V_{\beta 1}$ is the volume of the "interacting unit". By substituting in eq 2, it is then possible to show that

$$\left(\frac{K'_B}{S_B}\right) = \frac{\phi_{R_{n+1}}}{\phi_{R_n}\phi_{R_1}}\,\frac{n}{n+1} \tag{6}$$

so that a new equilibrium constant (K'_B/S_B) can now be defined in terms of known quantities. A similar procedure can be used for the acid units. Interaction between unlike species (e.g., solvent) then involve ratios of the molar volumes of the repeat unit and solvent molecules. In any event, it is not important to know the exact size of the interacting unit in setting up the equations for this particular problem, in that we will calculate our results in terms of the fraction of various hydrogen-bonded species present. The importance of this aside will arise later when we use equilibrium constants determined in other systems, which can then be modified for use here by multiplying by an appropriate ratio of molar volumes. A full discussion of the problem of defining appropriate (and transferable) equilibrium constants has been presented in a separate publication.[18]

Returning to our definitions of equilibrium constants, we come to the more complicated task of describing the types of complexes formed between carboxylic acid and amide functionalities. There are two types of bonds that, in principle, can be formed: between the C=O of the carboxylic acid and the NH of the amide group and between the OH of the carboxylic acid group and the carbonyl of the amide group, as illustrated in Figure 1. In this treatment we have ignored intramolecular hydrogen bonds, for reasons given above. These can be included, with the appropriate definition of equilibrium constants, if desired, but this does not affect our final conclusions.

To maintain a certain simplicity in the nomenclature, we will consider hydrogen-bonded chains of amide units to be directional, such that the first group in a chain has a free NH while the last group has a free carbonyl. We can then describe equilibria between amide groups and carboxylic acids in the following fashion:

$$A_1 + B_n \overset{K_{AB}}{\rightleftharpoons} AB_n \tag{7}$$

$$B_n + A_1 \overset{K_{BA}}{\rightleftharpoons} B_nA \tag{8}$$

where K_{AB} is not (necessarily) equal to K_{BA} and it is again assumed that both equilibrium constants are independent of n. The equilibrium constants K_{AB} and K_{BA} are defined as

$$K_{AB} = \frac{\phi_{A_1B_n}}{\phi_{A_1}\phi_{B_n}}\,\frac{nr}{(n+r)} \tag{9}$$

and

$$K_{BA} = \frac{\phi_{B_nA}}{\phi_{A_1}\phi_{B_n}}\,\frac{nr}{(n+r)} \tag{10}$$

where r is the ratio of the molar volumes of the acid and amide groups V_{A_1}/V_{B_1} and is necessary to account for the difference in size of the interacting species.

Finally, a hydrogen-bonded chain of amide groups with a carboxylic acid group at one end could still attach another acid group at the other extremity. If K_{AB} and K_{BA} are indeed independent of n, then

$$AB_n + A_1 \overset{K_{BA}}{\rightleftharpoons} AB_nA \tag{11}$$

$$A_1 + B_nA \overset{K_{AB}}{\rightleftharpoons} AB_nA \tag{12}$$

where

$$K_{BA} = \frac{\phi_{AB_nA}}{\phi_{AB_n}\phi_A}\,\frac{r(n+r)}{(n+2r)} \tag{13}$$

$$K_{AB} = \frac{\phi_{AB_nA}}{\phi_{B_nA}\phi_{A_1}}\,\frac{r(n+r)}{(n+2r)} \tag{14}$$

In order to prevent our model of the system from becoming even more complicated, we neglect the formation of additional hydrogen bonds between the "free" functionalities of the carboxylic acids that are bound by either their hydroxyl or carbonyls to amide groups and any other species. As we will see, our calculations and experimental results will demonstrate that for all reasonable values of the equilibrium constants, the number of acid–amide hydrogen bonds is small.

Having defined the types of hydrogen-bonded species that can be formed, we can now proceed to calculate the relationship between composition and the concentration of each of these species. This is simply done by noting that the volume fraction of amide groups present within a given sample, ϕ_B, and the volume fraction of carboxylic acid groups present within the sample, ϕ_A, are related to the volume fractions of the hydrogen-bonded complexes through the following equations:

$$\phi_B = \sum_{n=1}\phi_{B_n} + \sum_{n=1}\phi_{B_nA}\left(\frac{n}{n+r}\right) + \sum_{n=1}\phi_{AB_n}\left(\frac{n}{n+r}\right) + \sum_{n=1}\phi_{AB_nA}\left(\frac{n}{n+2r}\right) \tag{15}$$

$$\phi_{\mathrm{A}} = \sum_{n=1}^{2} \phi_{\mathrm{A}_n} + \sum_{n=1} \phi_{\mathrm{AB}_n}\left(\frac{r}{n + r}\right) + \sum_{n=1} \phi_{\mathrm{B}_n\mathrm{A}}\left(\frac{r}{n + r}\right) + \sum_{n=1} \phi_{\mathrm{AB}_n\mathrm{A}}\left(\frac{2r}{n + 2r}\right) \quad (16)$$

Of course, to be useful these summation terms have to be related to quantities that can be experimentally determined. As it turns out, these quantities can also be used to describe the thermodynamics of mixing acid and amide groups and are the volume fractions of the "monomers" ϕ_{B_1} and ϕ_{A_1} (i.e., those amide and acid groups that are not hydrogen bonded to any other species). This follows from Prigogine's demonstration that the macroscopic chemical potentials (μ_{A}, μ_{B}) are equal to the chemical potentials of the "monomer" molecules (μ_{A_1}, μ_{B_1}).[24] We have shown how the quantities ϕ_{B_1} and ϕ_{A_1} and the various equilibrium constants can be calculated from the fraction of free carbonyl groups (or, in principle, NH or OH groups) experimentally determined by infrared spectroscopy.[17-22] Our task therefore becomes the reorganization of the stoichiometric equations (15) and (16) in terms of these parameters. We proceed term by term and first calculate $\sum\phi_{\mathrm{B}n}$. This is most easily done by first defining the following equilibrium:

$$n\mathrm{B}_1 \overset{K_n}{\rightleftharpoons} \mathrm{B}_n \quad (17)$$

where

$$K_n = \frac{\phi_{\mathrm{B}_n}}{\phi_{\mathrm{B}_1}{}^n}\,\frac{1}{n} \quad (18)$$

The relationship between K_n and K_{B}, defined in eq 2, is

$$K_n = K_{\mathrm{B}}{}^{n-1} \quad (19)$$

noting that there are $n - 1$ hydrogen bonds in a chain of n amide units. Substituting in eq 18 we obtain

$$\phi_{\mathrm{B}_n} = nK_{\mathrm{B}}{}^{n-1}\phi_{\mathrm{B}_1}{}^n \quad (20)$$

For $K_{\mathrm{B}}\phi_{\mathrm{B}_1} < 1$ the following relationship holds:

$$\sum_{n=1} n(K_{\mathrm{B}}\phi_{\mathrm{B}_1})^{n-1} = \frac{1}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})^2} \quad (21)$$

so that

$$\sum_{n=1} \phi_{\mathrm{B}_n} = \frac{\phi_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})^2} \quad (22)$$

The second summation term is simplified in a similar manner:

$$\sum\phi_{\mathrm{B}_n\mathrm{A}}\frac{n}{(n + r)} = K_{\mathrm{BA}}\phi_{\mathrm{B}_n}\phi_{\mathrm{A}_1}\frac{n}{(n + r)}\,\frac{(n + r)}{nr} = \frac{K_{\mathrm{BA}}\phi_{\mathrm{A}_1}}{r}\phi_{\mathrm{B}_1}\sum n(K_{\mathrm{B}}\phi_{\mathrm{B}_1})^{n-1} = \frac{K_{\mathrm{BA}}\phi_{\mathrm{A}_1}}{r}\left(\frac{\phi_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})^2}\right) \quad (23)$$

Similarly

$$\sum\phi_{\mathrm{AB}_n}\frac{n}{(n + r)} = \frac{K_{\mathrm{AB}}\phi_{\mathrm{A}_1}}{r}\left(\frac{\phi_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})^2}\right) \quad (24)$$

In evaluating the final summation term in eq 15, care has to be taken not to count the ABA species twice. Use is made of

$$2\sum\phi_{\mathrm{AB}_n\mathrm{A}}\frac{n}{(n + 2r)} = \sum\phi_{\mathrm{AB}_n}\phi_{\mathrm{A}_1}K_{\mathrm{BA}}\,\frac{(n + 2r)}{(n + r)r}\,\frac{n}{(n + 2r)} + \sum\phi_{\mathrm{B}_n\mathrm{A}}\phi_{\mathrm{A}_1}K_{\mathrm{AB}}\frac{(n + 2r)}{r(n + r)}\,\frac{n}{(n + 2r)} \quad (25)$$

Substituting for ϕ_{AB_n} and $\phi_{\mathrm{B}_n\mathrm{A}}$ and proceeding as above, we obtain

$$\sum\phi_{\mathrm{AB}_n\mathrm{A}}\frac{n}{(n + 2r)} = \phi_{\mathrm{A}_1}{}^2\frac{K_{\mathrm{AB}}K_{\mathrm{BA}}}{r^2}\left(\frac{\phi_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})^2}\right) \quad (26)$$

The summation terms in eq 16 can be evaluated in a similar manner (by the relationship $\sum(\phi_{\mathrm{B}_1}K_{\mathrm{B}})^{n-1} = 1/(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})$), so that we obtain the following two equations:

$$\phi_{\mathrm{B}} = \frac{\phi_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})^2}\left[1 + \frac{K_{\mathrm{BA}}\phi_{\mathrm{A}_1}}{r} + \frac{\phi_{\mathrm{A}_1}{}^2K_{\mathrm{AB}}K_{\mathrm{BA}}}{r^2}\right] \quad (27)$$

$$\phi_{\mathrm{A}} = \phi_{\mathrm{A}_1} + 2K_{\mathrm{A}}\phi_{\mathrm{A}_1}{}^2 + \frac{\phi_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})}\left[\phi_{\mathrm{A}_1}K_{\mathrm{BA}} + \phi_{\mathrm{A}_1}K_{\mathrm{AB}} + \frac{2}{r}K_{\mathrm{AB}}K_{\mathrm{BA}}\phi_{\mathrm{A}_1}{}^2\right] \quad (28)$$

Competitive Equilibrium with Ether Groups. Ether groups are commonly found in a number of important poly(amic acid)s. Such groups are incapable of forming hydrogen bonds with one another, but can hydrogen bond to NH and OH groups. The equilibrium constants describing these interactions are defined in the same manner as above

$$K_{\mathrm{BE}} = \frac{\phi_{\mathrm{B}_n\mathrm{E}}}{\phi_{\mathrm{OE}}\phi_{\mathrm{B}_n}}\,\frac{nr'}{(n + r')} \quad (29)$$

$$K_{\mathrm{AE}} = \frac{\phi_{\mathrm{AE}}}{\phi_{\mathrm{OE}}\phi_{\mathrm{A}_1}}\,\frac{r''}{(1 + r'')} \quad (30)$$

where ϕ_{OE} is the volume fraction of the ether groups that remain "free" or not hydrogen bonded to any other group, and r' and r'' are the ratio of molar volumes $V_{\mathrm{E}}/V_{\mathrm{B}_1}$ and $V_{\mathrm{E}}/V_{\mathrm{A}_1}$, respectively. It is a straightforward matter to show that the additional terms introduced into eq 15 and 16 are

$$\frac{K_{\mathrm{BE}}\phi_{\mathrm{OE}}}{r'}\left[\frac{\phi_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})^2}\right] \quad \text{and} \quad \frac{K_{\mathrm{AE}}\phi_{\mathrm{OE}}\phi_{\mathrm{A}_1}}{r''} \quad (31)$$

respectively. To solve for the three unknown ϕ_{A_1}, ϕ_{B_1}, and ϕ_{OE}, a third mass balance equation is introduced

$$\phi_{\mathrm{E}} = \phi_{\mathrm{OE}} + \phi_{\mathrm{AE}}\left(\frac{r''}{1 + r''}\right) + \sum_{n=1}\phi_{\mathrm{B}_n\mathrm{E}}\left(\frac{r'}{n + r'}\right) \quad (32)$$

and reorganized in terms of the equilibrium constants and volume fractions of non-hydrogen-bonded units ("monomers") as above.

Interaction with Solvent. The equations can be expanded in exactly the same manner to account for the interactions of a solvent such a NMP with the acid and amide functional groups. Unfortunately, the concentration of residual solvent in cast films is not easily measured by FTIR, so that the calculation of the distribution of hydrogen-bonded species is not readily extended to this situation.

Calculations

In the preceding discussion equations characterizing the distribution of associated species have been described in considerable detail. In order to use these to obtain an exact quantitative description, the equilibrium constants would have to be known with a high degree of precision. For many of the proposed interactions, these data are simply not available and in any event precise descriptions are probably unwarranted by the limitations of the model.

Nevertheless, a broad picture of the pattern of hydrogen bonding can readily be obtained with a few simple and justifiable assumptions. First, we can obtain rough order of magnitude values for the equilibrium constants for self-association of like units, K_A and K_B. In recent work we have characterized hydrogen bonding in various ethylene–methacrylic acid copolymers and polyamides.[22,25,26] If we assume that the strength of the hydrogen bond between, for example, carboxylic acid pairs is about the same in the above copolymers and poly(amic acid)s (and a comparison of infrared frequency shifts indicates that they are) and note Pimentel and McClellan's observation that the enthalpy and entropy of many hydrogen bonds are linearly related,[10] then we can conclude that the free energy change for formation of a hydrogen-bonded pair, and hence the equilibrium constant, is thus also approximately equal. Of course, the equilibrium constant characterizing a particular functional group is defined in terms of the size of the (undefined) interacting unit. The relationship to an equilibrium constant defined in terms of the volume of a chemical repeat unit was given (for amide units) by eq 5 and 6. Similarly, for carboxylic acid groups we can write

$$K_\alpha / S_A = K_A \tag{33}$$

where K_α is an equilibrium constant defined in terms of an interacting segment, K_A is the equilibrium constant defined in terms of the chemical repeat unit, and S_A is the ratio of the volume of the chemical repeat unit to that of the interacting unit (i.e., the number of "segments" in the repeat unit). For polymers 1 and 2 with repeat units of different size we then have

$$K_A^{(1)} S_A^{(1)} = K_A^{(2)} S_A^{(2)} \tag{34}$$

hence

$$K_A^{(1)} = K_A^{(2)} \frac{S_A^{(2)}}{S_A^{(1)}} = K_A^{(2)} \frac{V_A^{(2)}}{V_A^{(1)}} \tag{35}$$

In effect, the different size of chemical repeat units affects the *number* of hydrogen bonds that can form, and this is accounted for in an "apparent" equilibrium constant. The interaction strength of those bonds that do form is the same, however, and is related to an equilibrium constant that is defined in terms of the interacting unit (K_α).

We can now use the definition of "apparent" equilibrium constants to transfer the values of equilibrium constants determined in one system to another with the same functional group by simply multiplying by the ratio of the molar volumes (or molar volumes of the chemical repeat units), provided that the strength of the interaction is the same in the two environments. We have determined that for an ethylene–methacrylic acid copolymer (44% acid units with a molar volume of about 197 units for an *average repeat*) the equilibrium constant K_A is about 57 000, reflecting the large free energy change associated with the formation of acid dimers.[22] We calculate an average molar volume of about 214 for the poly(amic acid) repeat of concern here, so that the equilibrium constant describing self-association of acids in this latter polymer should be of the order of 50 000. Using data obtained on an amorphous polyamide,[25,26] we similarly determined that the equilibrium constant for self-association of amides; K_B is in the range 150–250. The values for the interaction between acids and amides or acids and ethers are unknown, but our recent experimental work[19–22] suggests that they will be smaller than the values for self-association. It is not important to know these quantities precisely, however, because we can select a reasonable range for the values of the equilibrium constants and then plot the concentration of hydrogen-bonded species as a function of these equilibrium constant values. For example, if we let $K_B = 200$ and $K_{AB} = K_{BA} = 100$, then using eq 27 and 28 we can solve for ϕ_{A_1}, the volume fraction of acid units that are *not* hydrogen bonded, together with ϕ_{B_1}, the corresponding volume fraction of non-hydrogen-bonded amide groups. This is accomplished by choosing a value of K_A and any appropriate values of ϕ_A and ϕ_B. One choice is to let $\phi_A = \phi_B = 0.5$. The choice is immaterial to our purposes here, because the quantities we wish to determine are fractions. For example, Figure 2 shows the fraction of hydrogen-bonded acid pairs ($=\phi_{A_2}/\phi_A = 2K_A\phi_{A_1}^2/\phi_A$) plotted as a function of K_A. Obviously, any assumption concerning the size of the interacting unit cancels. The important point is that for typical values of K_A, in the

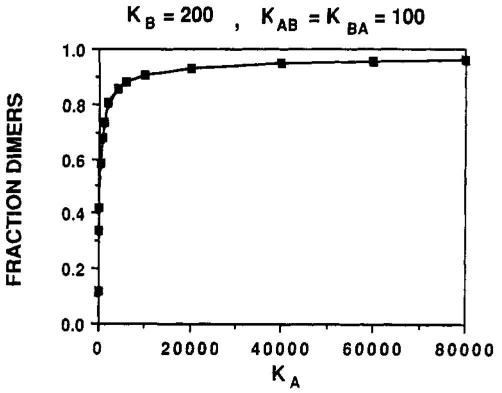


Figure 2. Plot of the fraction of carboxylic acid groups that are present as hydrogen-bonded pairs versus values of the equilibrium constant K_A describing self-association in the form of such acid pairs.

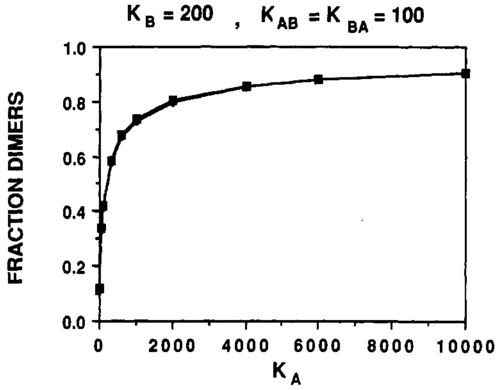


Figure 3. Expanded portion of Figure 2 in the range of values K_A = 0–10 000.

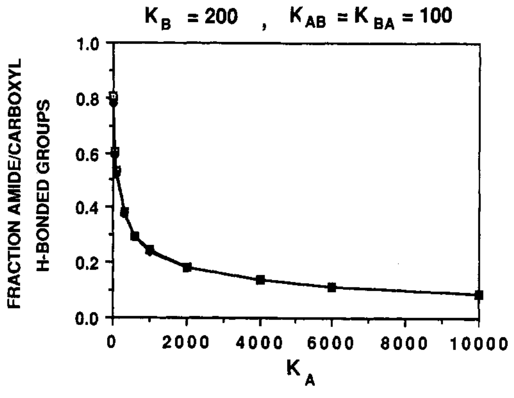


Figure 4. Plot of the fraction of carboxylic acid groups involved in acid/amide hydrogen bonds versus the value of the equilibrium constant describing self-association in the form of acid pairs.

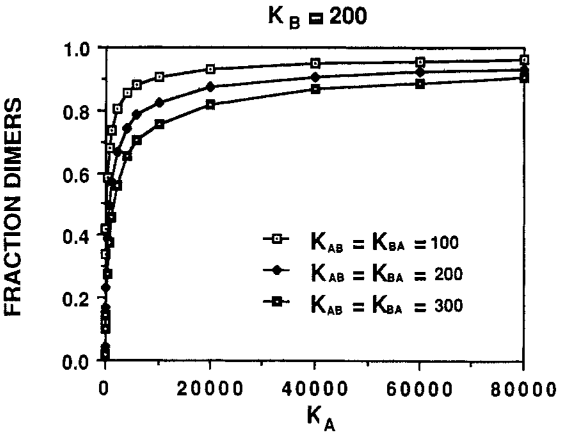


Figure 5. Plot of the fraction of carboxylic acid groups that are present as hydrogen-bonded pairs versus values of the equilibrium constant K_A.

range 40 000–60 000, the carboxylic acid groups are hydrogen bonded to one another in the form of characteristic pairs. In fact, K_A values of less than 2000 would have to be used to calculate appreciable fractions of acid/amide groups, as can be seen from Figures 3 and 4, which show an expanded portion of Figure 2 (K_A values in the range 0–10 000) and a plot of the fraction of acid groups present as acid/amide bonded species, respectively.

As an aside, it may at first seem that K_A values in the range 50 000 are extremely large and unlikely, particularly when compared to the values used for self-association of amides (~200). It should be noted, however, that the natural logarithm of this number is related to free energy per hydrogen bond. In turn, this quantity is related to corresponding enthalpy and entropy changes, the former of which is significantly larger for formation of acid dimers[9] than for amide groups (~7 or 8 kcal/mol versus 4 or 5 kcal/mol).

Finally, the curves shown above are obviously dependent upon the assumed values of K_{AB} and K_{BA}. Even if the formation of acid/amide hydrogen bonds were to occur with the same free energy change as amide/amide bonds (unlikely, in our opinion, given the equilibrium constant data than can be found in the literature[20-22,27]), our general conclusions are unaltered. Using values between 100 and 300 results in the curve shown in Figure 5, where again for values of K_A larger than about 10 000 more than 80% of the carboxylic acid functional groups are present as hydrogen-bonded pairs. We will now turn our attention to spectroscopic measurements as a test of these general conclusions.

Results and Discussion

There are two regions of the infrared spectrum that are particularly sensitive to hydrogen bonding: between 1800 and 1600 cm^{-1}, where C═O stretching modes appear, and the entire region between 3800 and 1800 cm^{-1}, characteristic of NH and OH stretching modes. In many simple compounds, hydrogen-bonded NH and OH modes usually have broad bands centered near 3300 cm^{-1}. This is a characteristic of so-called "weak" hydrogen bonds, however. As the strength of a hydrogen bond increases to the "intermediate" level, typical of carboxylic acid pairs, then the stretching mode shifts to lower frequencies (centered near 3000 cm^{-1}) and so-called satellite bands appear (due to overtones and combinations that are intensity enhanced by Fermi resonance), superimposed upon the broad fundamental profile. Finally, "strong" hydrogen bonds result in intriguingly peculiar spectra, where the fundamental can split into (usually) three components, with the lowest frequency band often found near 1900 cm^{-1}. (These types of hydrogen-bonded systems are described in ref 28–31).

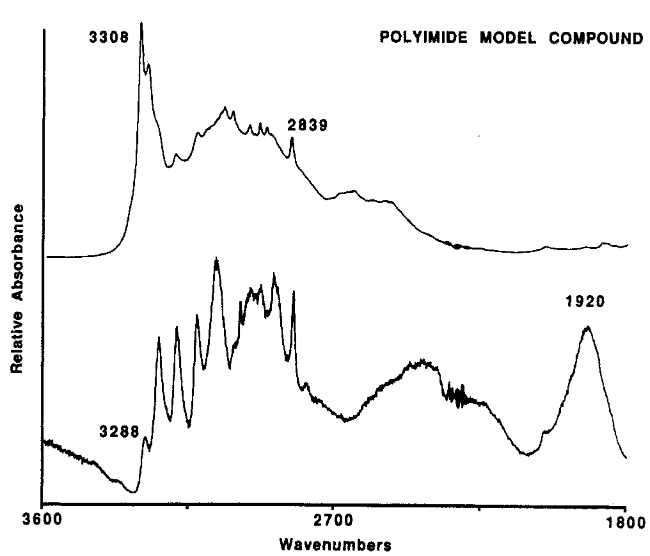
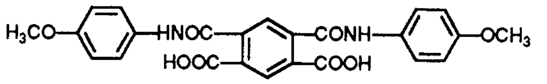


Figure 6. FTIR spectra between 3600 and 1800 cm^{-1} of (top) a solvent-free amic acid model compound and (bottom) a sample hydrogen bonded to residual solvent.

All of these characteristics can be observed in the spectra of amic acids, greatly complicating the interpretation of the OH and NH stretching modes. For example, in the 3800–1800-cm^{-1} region of the spectrum of the following model compound, obtained by precipitating the product of reacting PMDA and p-anisidine from NMP into water with subsequent washing to remove residual solvent, a strong N–H stretching mode, split into a doublet, appears near 3300 cm^{-1}, as can be seen in Figure 6. A broad band centered near 3000 cm^{-1} can be assigned to hydrogen-bonded carboxylic acid pairs, while "satellite" bands appear near 2600 cm^{-1}. NMP forms strong hydrogen bonds with carboxylic acid groups, and in samples where residual solvent has not been removed, three characteristic very broad bands centered near 2900, 2400, and 1900 cm^{-1} can be observed, as also shown in Figure 6. In addition, a number of bands beteen 3200 and 3000 cm^{-1} are apparent. Clearly, such complex spectra can only be interpreted in the broadest manner. Although the positions of the bands in the solvent-free spectrum are consistent with predominantly amide/amide and carboxylic acid/carboxylic acid types of hydrogen bonds, there are enough "splittings" and "satellite" bands to suggest that amide/carboxylic acid hydrogen bonds, formed inter- or intramolecularly, could also be present.



Fortunately, the carbonyl stretching region of the spectrum is less ambiguous. Figure 7 shows the spectrum of the amic acid model compound, washed with water to remove solvent. Two C═O stretching bands are apparent, near 1700 and 1640 cm^{-1}, classic group frequencies for hydrogen-bonded carboxylic acid pairs and amide groups self-associated in the form of chains. There is little evidence for hydrogen bonds between carboxylic acids and amides. These would result in the appearance of bands at a higher frequency than 1705 cm^{-1}. For example, if the OH group of the carboxylic acid were hydrogen bonded to the amide carbonyl, the resulting nonbonded carboxyl C═O mode would shift toward 1750 cm^{-1}, the characteristic frequency of "free" groups. If the carboxyl C═O were hydogen bonded to the amide N—H, then a band between

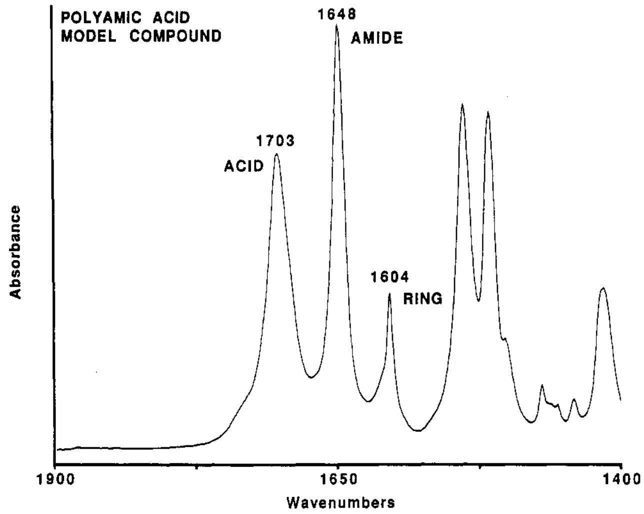


Figure 7. Carbonyl stretching region of the infrared spectrum of an amic acid model compound.

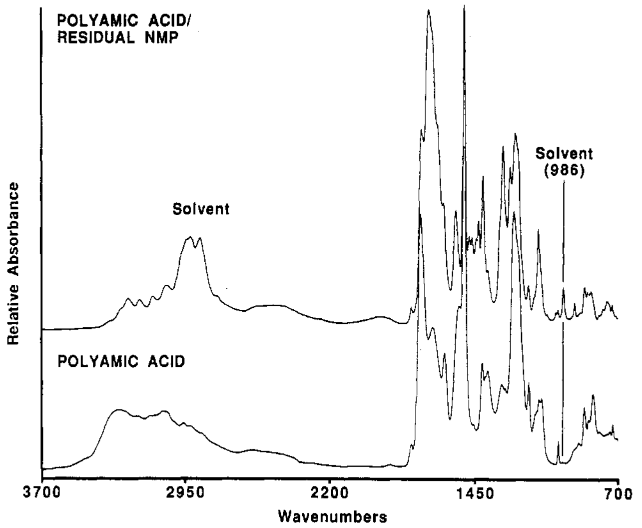


Figure 8. FTIR spectrum of a washed poly(amic acid) film compared to the spectrum of solvent (NMP).

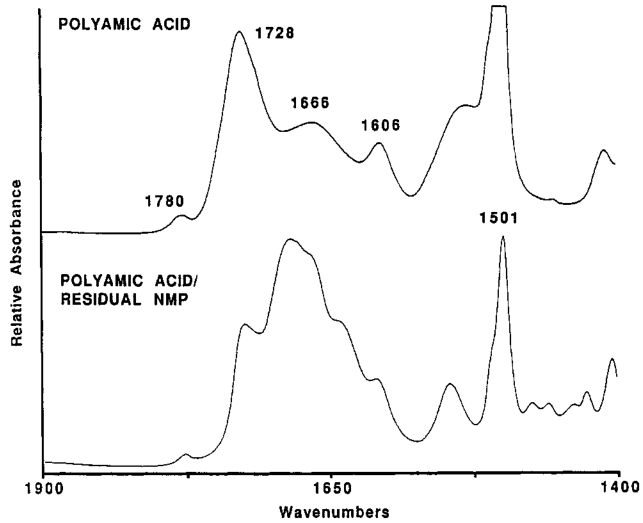


Figure 9. Carbonyl stretching region of the infrared spectrum of a poly(amic acid). Bottom, cast film containing residual hydrogen-bonded solvent; Top, film washed with water to remove solvent.

1750 and 1705 cm^{-1} would again appear, because the strength of such N—H/C=O interactions are less than those in carboxylic acid hydrogen-bonded pairs.[10] Accordingly, these spectroscopic results are in good agreement with the theoretical predictions presented above.

In films with a residual strongly hydrogen-bonding solvent such as NMP, bands shifted to lower frequencies can be observed, but not to the exclusion of bands assigned to self-associated species described above. We will not reproduce spectra here, since Brekner and Feger[8] have covered this ground, showing four C=O bands in this region of the spectrum. Furthermore, on the basis of scattering data, Russell[32] argues that there is periodic aggregation of poly(amic acid) chain segments in solvent-containing films, analogous to a polymer mixture at the initial stages of spinodal phase separation. Clearly, there is an equilibrium distribution of hydrogen-bonded species in solvent-cast films, and Brekner and Feger[7,8] have strong evidence for the presence of 2/1 complexes in initially cast films. In model compounds, at least, these authors have also shown that the strongly bound NMP is largely removed at temperatures below the onset of imidization (although there is some overlap). The rate of removal of residual solvent during curing will thus greatly affect the distribution of hydrogen-bonded species present. It would clearly be of interest to calculate the stoichiometry of hydrogen bonding to solvent by our association model and extend the treatment to a calculation of polymer/solvent phase behavior. This requires that we obtain values of the equilibrium constants describing the interaction of NMP with carboxylic acid and amide functional groups, however, and these are not presently available.

One complication has to be kept in mind. The amide and carboxylic acid groups in an individual molecule, or the repeat unit of a poly(amic acid), are spatially close together. If there is sufficient molecular mobility when solid samples are being formed, then these functional groups can hydrogen bond to their own kind. In partially cured samples, particular carboxylic acids and amide groups may become isolated from potential partners of the same type and will then hydrogen bond to whatever appropriate group is available. In certain amic or poly(amic acid)s this will also include the ether functional group, which can hydrogen bond to NH or carboxylic acid OH groups. We have observed that in our commercialy obtained sample of poly(amic acid) there is a small degree of imidization in the as-received form. A typical spectrum of a dried cast film, where solvent has been removed by washing with water, is shown in Figure 8 (also shown in this figure is the spectrum of NMP, to demonstrate that solvent bands have been practically completely removed). The carbonyl region of the spectrum is shown in Figure 9, where the spectra of the washed poly(amic acid) is compared to that of a film containing residual NMP. The bands near 1780 and 1730 cm^{-1} are due to the presence of some imide groups, but it is also apparent that the residual carboxylic acid and amide functionalities have broadened and shifted to higher frequency. At this point the distribution of hydrogen-bonded species present will depend upon the number of imide or other linkages formed, whether or not these are randomly located, as well as the concentration of residual solvent (if any). These points will be explored in the following paper.

Conclusions

In solvent-free amic acids and poly(amic acid)s the pattern of hydrogen bonding is largely association between functional groups of the same type; that is, carboxylic acid hydrogen-bonded pairs and chains of hydrogen-bonded amide groups are the principal species present. Solvents such as NMP can strongly hydrogen bond to these groups and break this pattern, to the extent that in "dried" films residual solvent is still present and there is a complex equilibrium of self-associated and polymer/solvent complexes present.

Registry No. (PMDA)(4,4′-oxydianiline) (copolymer), 25038-81-7; (PMDA)(4,4′-oxydianiline) (SRU), 9043-05-4.

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FTIR Studies of Polyimides: Thermal Curing

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ABSTRACT: In this study the thermal curing of poly(amic acid) films is considered. Analysis of the carbonyl stretching region of the infrared spectrum indicates that in addition to ring-closed imides, some intermolecular links are formed. The relative proportion of these species changes with conditions of cure.

Introduction

Infrared spectroscopic studies of polyimide films can be roughly divided into two categories. In the first, ring closure is implicitly assumed and various bands used as a measure of the degree of imidization.[1-5] The second category involves the use of infrared spectroscopy as a tool for identifying the species actually formed (for example, see ref 6–11). In this context, a distinction between the products obtained by chemical as opposed to thermal curing can also be made. Because normal coordinate calculations of polyimide molecules have yet to be reported, identification of structures has been largely based on group frequency assignments of the characteristic carbonyl stretching modes between 1600 and 1800 cm^{-1}.[6,7]

In this study we will also rely on this region of the spectrum to identify the products formed upon thermal curing. Although similar studies have been reported previously, most of these used "thick" (in infrared spectroscopic terms) films and dispersive instruments. As we will show, the sampling and data analysis advantages of FTIR instruments provide new information.

Experimental Section

The poly(amic acid) used in this study is a poly(pyromellitic dianhydride oxydianiline) obtained from Du Pont. Thin films ($\sim$1 μm) were prepared by casting from solutions of NMP (*N*-methylpyrrolidinone) onto KBr windows. Samples were cured at low temperatures by using a Micro Star heating cell placed in the sampling compartment of the spectrometer. Samples cured at high temperatures (about 10-μm-thick films) were sprayed onto ceramic substrates and cured in ovens at the IBM laboratories in Endicott, NY. Various curing protocols were used and these are described in the body of the text.

Spectra were recorded on a Digilab FTS 60 spectrometer at a resolution of 2 cm^{-1}. Samples of "thick" films ($\sim$10 μm) were prepared by taking a small piece ($\sim$1–2 mm) and placing it on top of a KBr underlayer ($\sim$300 mg) in a diffuse reflectance cup. The diffuse reflectance spectra were then obtained in the usual fashion. Spectra of model compounds were obtained by dispersing

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