

A Methodology of Selecting Greener Solvent Mixtures for Preparing Soluble Polyimide Precursors

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論文内容要約

Chapter 1: Aromatic polyimides (API) are widely used in engineering plastics for electronic, automotive and aerospace industries due to outstanding performances. API requires homogeneous precursor solutions, which is known as poly(amic acid) (PAA) solution, to realize specific forms and functionalities. Homogeneous PAA solution studied in this work is synthesized by reaction of pyromellitic dianhydride (PMDA) with 4,4'-oxydianiline (ODA) in presently used pure hydrogen-bond acceptor (HBA) solvents such as *N*-methyl-2-pyrrolidone (NMP) that allow preparation of PAA concentration up to 5-15 wt% in the solution. However, presently used pure HBA solvents are hazardous and nonrenewable. The goal of this work is to synthesize homogeneous PAA solutions in green solvents that are safe and renewable.

Chapter 2: To address this problem, hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) mixtures such as tetrahydrofuran (THF)-methanol (MeOH) and THF-ethanol (EtOH) have been used for replacement of hazardous solvents. The advantage of using solvent mixtures is adjustability of their physicochemical properties. However, the selections of solvent mixtures and their compositions are not well understood. The objectives of this thesis were to develop a methodology for selecting green solvent mixtures and their favorable compositions used for preparing homogeneous PAA solutions and to validate that by varying experimental results.

Chapter 3: From experimental preparation of PAA solutions in pure 33 solvents and 17 solvent mixtures, the methodology for selecting green solvent mixtures used for preparing homogeneous PAA solutions was proposed and consisted of six steps as shown in Figure 1. For the (i) and (ii) steps of the methodology, solvent mixtures were listed through a popular health-judged level (Glaxo-smith-Kline, GSK), solubility parameter (δ) window along with consideration of HBA-HBD molecular characteristics, where solvent mixtures have δ values within the δ window (20.5-29.2 MPa^{0.5}). Although the δ parameter is useful to define a target solubility window, it lacks detailed description of molecular interactions that can be

provided by “Indicator-centric” Kamlet-Taft solvatochromic (K-T) parameters consisting of π_{IC}^* (polarity), β_{IC} (basicity), and α_{IC} (acidity) contributions obtained from solvatochromic indicators.

In the (iii) step of the methodology, the K-T parameters of pure solvent and identified solvent mixtures were assessed. Homogeneous PAA solutions are obtained in pure HBA solvents that have high polarity ($\pi_{IC}^* > 0.87$) and high basicity ($\beta_{IC} > 0.64$) because the reason is considered to be necessary to induce the dissolution of PAA by specific interactions.

Thus, the idea for selecting solvent mixture is a combination of an HBD solvent having high β_{IC} and low π_{IC}^* values (e.g. MeOH and EtOH) with an HBA solvent having low β_{IC} and high π_{IC}^* values (e.g. γ -valerolactone (GVL) and γ -butyrolactone (GBL)).

In the (iv) step of the methodology, due to non-ideality, the K-T parameters for the solvent mixtures were measured to assess whether the solution properties in terms of β_{IC} and π_{IC}^* parameters showed the trend of moving towards the PAA-soluble region of the pure HBA solvents ($\beta_{IC} > 0.64$, $\pi_{IC}^* > 0.87$). The enhancement in terms of β_{IC} and π_{IC}^* parameters is due to a synergistic effect from the formation of HBA-HBD complex solvent molecules via hydrogen donor/acceptor.

In the (v) step of the methodology, PAA polymerizations were also carried out in solvent mixtures to check for homogeneous reaction and to validate the δ window and K-T parameters. Homogeneous PAA solutions could be obtained from HBA-HBD solvent-pair mixtures when their δ values are within 21-29 MPa^{0.5} and their K-T parameters were π_{IC}^* (> 0.67) and β_{IC} (> 0.61) for non-aqueous solutions and π_{IC}^* (> 0.68) and β_{IC} (> 0.59) for aqueous solutions.

In the (vi) step of the methodology, if homogeneous reaction occurred, the polymer properties were analyzed by FT-IR, ¹H-NMR, TGA, and GPC methods and were compared to those of commercial PAA solution as reference data. Renewable and safe solvent mixtures, GVL-EtOH, GVL-water, and GBL-water gave homogeneous precursor solutions that were comparable with commercial solutions prepared with NMP.

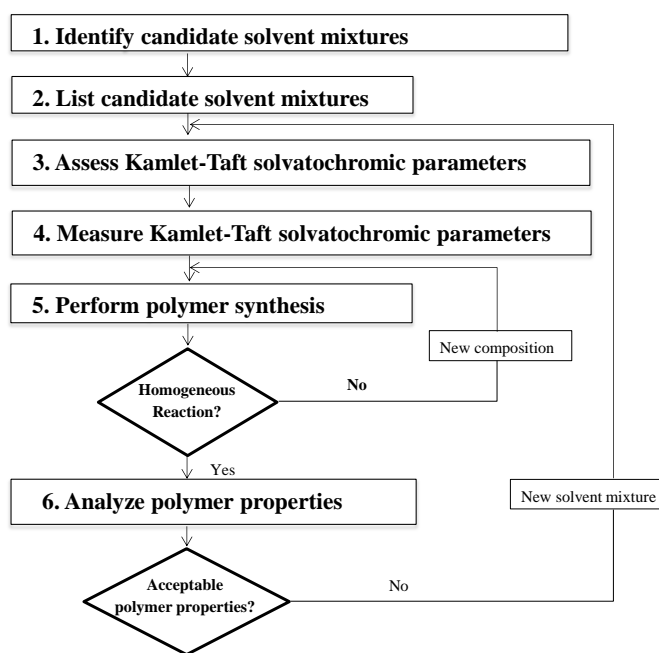


Fig.1 Methodology for selecting solvent mixtures

Chapter 4: Since PAA polymer and ODA monomer are solvated only in pure HBA solvent, homogeneous PAA solutions require HBA-rich composition of HBA-HBD solvents because dissolution, dispersion and reaction occur faster in HBA-rich solvent conditions than in HBA-poor solvent conditions. This result was verified by observing dissolution, dispersion and reaction of PAA solution with time dependence (temporal variation of solution absorption) using UV-Vis technique.

In addition, ODA monomer has strong specific interactions with HBA solvent in HBA-HBD solvent mixtures, while the solvatochromic parameter for measuring acidity (α_{IC}) monomer has strong specific interactions with HBD solvent in HBA-HBD solvent mixtures that cause difference in local composition. Thus, “solute-centric” K-T parameters for the solvent environment around the monomer are different from indicator-centric K-T parameters because K-T parameters depend on local compositions. Model for determining solute-centric K-T parameters was proposed model by incorporates spectroscopically-determined local composition around the ODA monomer using preferential solvation model and K-T parameters of the pure solvent and mixed-solvent complex HBA-HBD molecule.

Chapter 5: The proposed methodology for selecting green solvent mixtures is effective to identify the new solvent mixtures for preparing soluble polyimide precursor solution and other polymer precursor solutions used in engineering plastics. The proposed procedure and model for determining solute-centric Kamlet-Taft solvatochromic parameters can possibly be applied to other solute-mixed-solvent systems that have strong specific interactions.