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Replacement of Hazardous Chemicals Used in Engineering Plastics with Safe and Renewable Hydrogen-Bond Donor and Acceptor Solvent-Pair Mixtures

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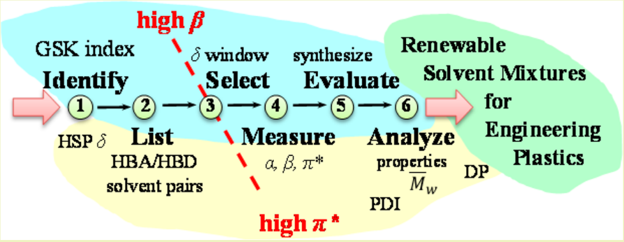
Supporting Information

ABSTRACT: Mixtures of safe and renewable solvents can replace hazardous solvents presently being used in the manufacture of engineering plastics. In this work, a methodology is proposed for identifying solvent-pair mixtures for preparing polymer precursors, with poly(amic acid) (PAA) being studied as an example. The methodology uses a chemical safety index, Hansen solubility parameters and Kamlet−Taft solvatochromic parameters of the pure and solvent-pair mixtures to identify hydrogen bond acceptor (HBA)−hydrogen bond donor (HBD) solvent-pair combinations. Ten replacement solvent-pairs for PAA syntheses identified were cyclohexanone−methanol, cyclohexanone−ethanol, cyclopentanone−methanol, cyclopentanone−ethanol, γ-butyrolactone−methanol, γ-butyrolactone−ethanol, γ-butyrolactone−water, γ-valerolactone−methanol, γ-valerolactone−ethanol, and γ-valerolactone−water. Homogeneous PAA solutions could be obtained from HBA−HBD solvent-pair mixtures when their solubility parameters were within 21−29 $\text{MPa}^{0.5}$ and their Kamlet−Taft solvatochromic parameters were π^* (>0.67) and β (>0.67) for nonaqueous solutions and π^* (>0.68) and β (>0.59) for aqueous solutions. Replacement solvent-pairs, γ-valerolactone−ethanol, γ-valerolactone−water, and γ-butyrolactone−water gave homogeneous precursor solutions that were comparable with commercial solutions prepared with *N*-methyl-2-pyrrolidone. The proposed methodology and reported solvatochromic parameters make it is possible to identify other solvent-pair mixtures and new solvent-pairs for preparing polymer precursor solutions used in engineering plastics.



KEYWORDS: *Polymer, Green solvents, Precursor solution, Polyimide, Solvatochromic parameter*

INTRODUCTION

Many solvents used in the manufacture of engineering plastics are hazardous and nonrenewable, because the required polymer precursors must be homogeneous solutions to realize specific forms and functionalities.[1] In this work, a methodology is presented to replace these solvents by using hydrogen bond acceptor (HBA)−hydrogen bond donor (HBD) solvent-pair mixtures that are safe and renewable. As an example of the methodology, precursors of aromatic polyimides (API) are studied, because they are widely used in engineering plastics.[2−7]

APIs are generally prepared by a two-step process.[2,7,8] In the first step of API synthesis, a solution containing a polyimide precursor, which is known as soluble poly(amic acid) (PAA), is prepared by reaction between an aromatic diamine and an aromatic dianhydride at 20−40 °C in large amounts of solvent.[2] Pure solvents being used include *N*-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMA), or dimethylformamide (DMF) that contain about 5−15 wt % PAA in the solution.[2]

However, there are a limited number of solvents that can be used for obtaining homogeneous PAA solutions and most of the solvents are toxic, dangerous, or flammable as ranked by the GSK solvent selection guide.[11,12] Replacement of presently used solvents with greener solvents or renewable solvent mixtures could lead to safe and sustainable chemical processes for preparing polymer and engineering plastics.[9,10,13]

One method to assess potential replacement solvents is by considering the GSK health level[11] and the Hansen solubility parameter (δ).[14,15] Figure 1 and Table S1 (Supporting Information) show the GSK level for health effects (L = low risk) along with the solubility parameter for pure solvents. According to solubility parameter theory,[14] pure solvents (Figure 1) that are within the solubility parameter window of pyromellitic dianhydride (PMDA) and 4, 4′-oxidianiline (ODA) monomers and PAA polymer (≈21−29 $\text{MPa}^{0.5}$) should be suitable for preparation of homogeneous PAA solutions.

Of the presently used pure solvents for preparing homogeneous PAA solutions, only dimethyl sulfoxide (DMSO) and pyridine (Pyr) have a moderate GSK health

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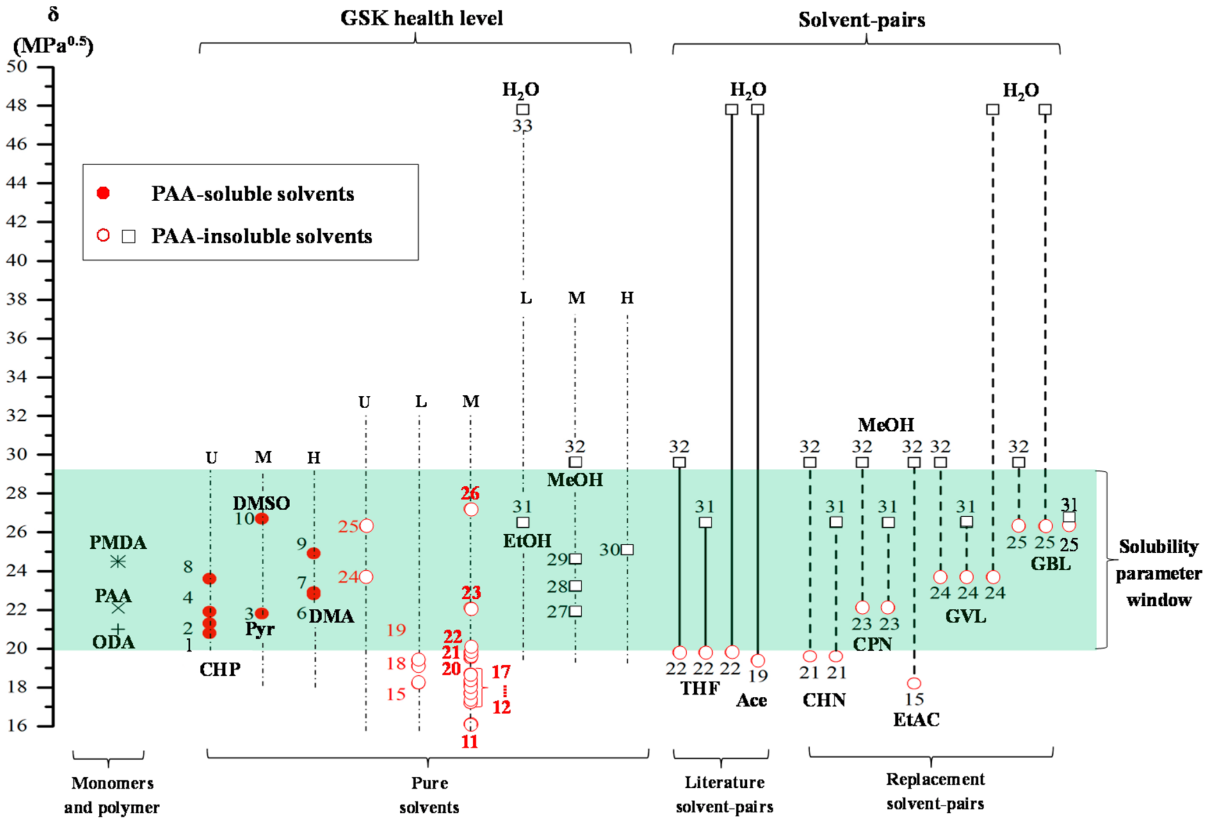

Figure 1. Pure solvents and solvent-pairs that have been used in the literature and those that are proposed in this work for preparing homogeneous solutions of poly(amic acid) (PAA) precursor. The solubility parameter (δ) is given for each solvent and for pyromellitic dianhydride (PMDA) and 4,4′-oxidianiline (ODA) monomers, and poly(amic acid) (PAA) polymer. GSK health level according to GSK solvent selection guidelines[11] is shown for pure solvents (L = low risk, M = moderate risk, H = high risk, U = unknown). Symbols: red ●, PAA soluble in hydrogen bond acceptor (HBA) solvents; ○, PAA insoluble in HBA solvents; □, PAA insoluble in hydrogen bond acceptor (HBD) solvents. Filled symbols show solvents that form homogeneous PAA solutions (PAA-soluble). Unfilled symbols show solvents that form heterogeneous PAA solutions (PAA-insoluble). Solvent list: 1 = *N*-cyclohexyl-2-pyrolidone (CHP), 2 = diethyl acetamide (DEA), 3 = pyridine (Pyr), 4 = diethyl formamide (DEF), 5 = hexamethyl phosphoramide (HMPA), 6 = dimethylacetamide (DMA), 7 = *N*-methyl-2-pyrrolidone (NMP), 8 = *N*-acetyl-2-pyrrolidone (NAP), 9 = dimethylformamide (DMF), 10 = dimethyl sulfoxide (DMSO), 11 = acetonitrile (ACN), 12 = cyclopentyl methyl ether (CPME), 13 = eucalyptol (Euc), 14 = 2-methyl tetrahydrofuran (MTHF), 15 = ethyl acetate (EtAc), 16 = 2-pentanone (MPK), 17 = dimethyl carbonate (DMC), 18 = 2-butanone (MEK), 19 = acetone (Ace), 20 = anisole (Ans), 21 = cyclohexanone (CHN), 22 = tetrahydrofuran (THF), 23 = cyclopentanone (CPN), 24 = γ-valerolactone (GVL), 25 = γ-butyrolactone (GBL), 26 = propylene carbonate (PPC), 27 = 1-pentanol (PeOH), 28 = 1-butanol (BuOH), 29 = 1-propanol (PrOH), 30 = 2-methoxyethanol (MxOH), 31 = ethanol (EtOH), 32 = methanol (MeOH), and 33 = water (H_2O).

level, while other solvents shown in Figure 1 have a high or unknown GSK health level. Other pure solvents can be considered using the GSK health level and the δ value, but many of these solvents do not allow homogeneous solutions of PAA to be prepared.

All presently known solvents for preparing homogeneous PAA solutions are hydrogen bond acceptors (filled circles, Figure 1).[2] Solvent-pairs such as water–tetrahydrofuran (THF), water–acetone, methanol (MeOH)–THF, and ethanol (EtOH)–THF have been proposed in the literature[16−20] and as shown in Figure 1, these allow coverage of the solubility parameter window of PMDA and ODA monomers and the PAA polymer. However, THF-containing solvent-pairs shown in Figure 1 may have safety issues when used on a practical scale due to possible formation of peroxides associated with handling THF.[50] The importance of the solvent characteristics has great impact on the greenness of a chemical process.[10,13,21,22]

In this work, we consider the following solvent-pairs that consist of the combination of a hydrogen bond donor solvent and a hydrogen bond acceptor solvent as follows: (**i**) methanol–cyclohexanone (CHN); (**ii**) methanol–cyclopentanone (CPN); (**iii**) methanol–ethyl acetate (EtAc); (**iv**) methanol–γ-valerolactone (GVL); (**v**) methanol–γ-butyrolactone (GBL); (**vi**) ethanol–CHN; (**vii**) ethanol–CPN; (**viii**) ethanol–GVL; (**ix**) ethanol–GBL; (**x**) water–GVL; (**xi**) water–GBL. Although MeOH, CHN, and CPN all have moderate GSK health levels, GVL and GBL have not been ranked according to GSK health levels, but can be derived from renewable resources[23−25] and can be expected to have low GSK health levels[26] and low toxicity,[24,27−29] especially the solvent GVL.

Molecular characteristics of the solvents (hydrogen bond acceptor (HBA)–hydrogen bond donor (HBD)), and reactivity characteristics of the solvent-pairs that limit side reactions are important in considering possible replacements. Because the miscibility ranges of the solvent-pairs are a critical technical constraint, the selection of the solvent-pairs and their mixture composition is challenging.

Although the solubility parameter is useful to define a target solubility window, it lacks detailed description of molecular interactions that can be provided by Kamlet–Taft solvatochromic (K-T) parameters.[15,28,30,31] In this work, K-T parameters are used in the methodology for selecting the solvent-pair mixtures.

Figure 2 shows the methodology developed in this research for selecting solvent-pair mixtures that have favorable characteristics for preparing polymer precursor solutions. As shown in Figure 2 (step 1), initial solvents were identified through the GSK health level, solubility parameter window along with consideration of molecular characteristics, reactivity, and probable miscibility ranges. A list of about ten replacement solvent-pairs (Figure 1) was formulated (step 2). The Kamlet−Taft solvatochromic parameters of selected solvent-pair mixtures were assessed and measured (steps 3 and 4, Figure 2) and polymerizations were carried out (step 5, Figure 2) to check for homogeneous reaction. Then, if homogeneous reaction occurred, the polymer properties were analyzed (step 6, Figure 2).

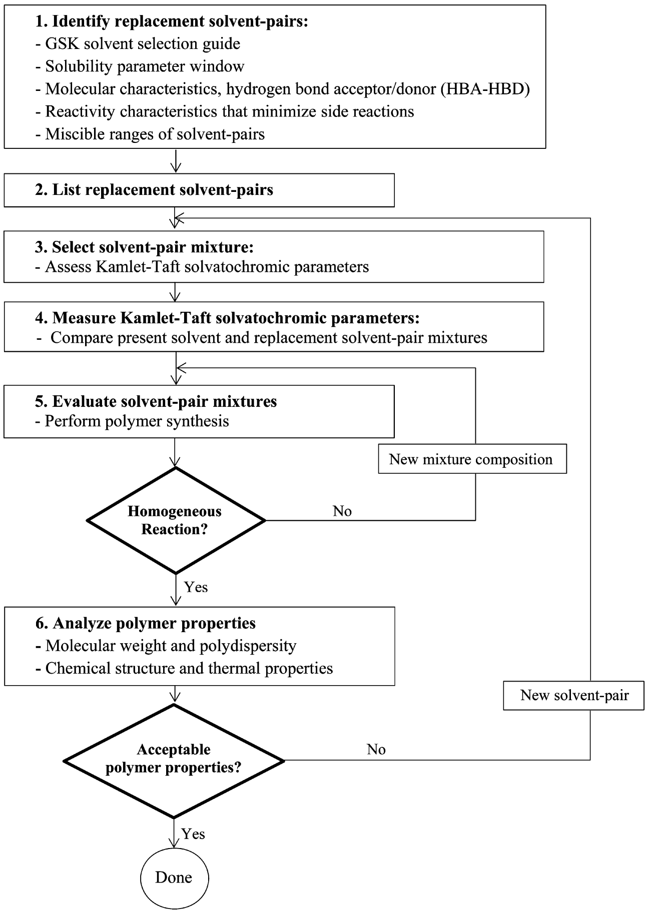

Figure 2. Methodology of selecting replacement solvent-pairs for preparing polymer precursor solutions via homogeneous reaction.

The objective of this work was to apply the methodology shown in Figure 2, so that safe and renewable solvent-pairs could be identified and evaluated for preparing homogeneous polymer precursor solutions. In this work, poly(amic acid) (PAA) was chosen as an example of a polymer precursor solution used in the manufacture of an engineering plastic to illustrate the methodology.

■ EXPERIMENTAL SECTION

Materials. Monomers of pyromellitic dianhydride (97%) and 4,4′-oxidianiline (99%) were purchased from Sigma-Aldrich Co. and Wako Chemical Co. Ltd. (Japan), respectively. Pyridine (99%), dimethylacetamide (99%), *N*-methyl-2-pyrrolidone (99%), dimethylformamide (HPLC grade), dimethyl sulfoxide (99%), acetonitrile (99%), ethyl acetate (99.8%), 2-pentanone (98%), dimethyl carbonate (98%), 2-butanone (98%), acetone (99%), cyclohexanone (95%), tetrahydrofuran (HPLC grade), cyclopentanone (95%), *γ*-butyrolactone (99%), pentanol (98%), butanol (98%), propanol (98%), 2-methoxyethanol (98%), ethanol (99.5%), methanol (99.8%), and distilled water (HPLC grade) were obtained from Wako Chemical Co. Ltd. Cyclopentyl methyl ether (99.9%), eucalyptol (99%), 2-methyltetrahydrofuran (99%), anisole (99.7%), *γ*-valerolactone (99%), and propylene carbonate (99.7%) were purchased from Sigma-Aldrich Co. All chemicals were used as received without further purification for the experiments of preparing the homogeneous poly(amic acid) solutions. Commercial poly(amic acid), pyromellitic dianhydride-*co*-4,4′-oxidianiline, (CAS no. 25038-81-7) used for comparison was a 15 wt % solution in *N*-methyl-2-pyrrolidone (Sigma-Aldrich Co). Chemical structures of the monomers and polymer are given in the Supporting Information (Figure S1).

Kamlet−Taft solvatochromic parameters of the replacement solvent-pairs (Figure 1) were measured using the solvatochromic indicators (Table S2 in the Supporting Information). The *N*,*N*-dimethyl-4-nitroaniline (98%) and 4-nitroanisole (98%) were purchased from TCI chemical Co. Ltd. (Japan). The 4-nitroaniline (99%), 4-nitrophenol (99.5%), and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate (90%) were obtained from Sigma-Aldrich Co. The solvatochromic indicators listed in Table S2 of the Supporting Information were used without further purification and their molecular structures are illustrated in the Supporting Information (Figure S2).

The chemicals and purities used in the Kamlet−Taft solvatochromic (K-T) parameter measurements were different from those used in PAA syntheses. In the K-T measurement, methanol (HPLC grade), ethanol (HPLC grade), and distilled water (HPLC grade) were purchased from Wako Chemical Co. Ltd. Cyclohexanone (99.8%), cyclopentanone (99.8%), *γ*-valerolactone (99%), and *γ*-butyrolactone (99%) were obtained from Sigma-Aldrich Co. All solvents were used as received without further purification.

For GPC analysis, dimethylformamide (HPLC grade) used as the mobile phase was obtained from Wako Chemical Co. Ltd. The additives for the mobile phase, lithium bromide (99.5%) and phosphoric acid (99%) were purchased from Wako Chemical Co. Ltd. and Sigma-Aldrich Co., respectively.

Measurement of Solvatochromic Parameters. Mixtures were prepared by mass using a microbalance (Mettler Toledo, model ax 504) with an uncertainty of $\pm 4 \times 10^{-4}$ g. The concentrations of the indicators were adjusted to be 5×10^{-5} mol·dm^{-3}, except for indicator number 5 (Table S2 of the Supporting Information) that was prepared at 1×10^{-4} mol·dm^{-3}. Spectral measurements were performed using a UV−vis spectrophotometer (Jasco, model V-530) with a spectral bandwidth of 2 nm in a 1 cm path length of quartz cell of with an encapsulation case. Temperature was held constant at temperature 25 ± 0.1 °C using a temperature controller (Jasco, ETC 505). The wavenumber interval of UV−vis analyses was 0.2 nm with replicates being the average of three scans. The wavelength reading of the spectrophotometer was calibrated using a UV−vis standard, holmium (III) in perchloric acid according to the procedure for Standard Reference Material (SRM) from NIST.[32] The uncertainty of the wavelength measurement was ±0.8 nm.

The π^*, β, and α parameters were obtained by using the relationships in Table S2 of the Supporting Information.[33,34] The maximum wavelength of the indicators (λ_{max}) was determined with numerically smoothed curves for the first-order derivative of absorption using Origin software (Microcal, version 9.1).[35]

Preparation of PAA Solutions. Poly(amic acid) (PAA) solutions in this work were prepared at a concentration of 5 wt %. Reactions of 5 wt % of PAA solutions in the pure solvents, literature solvent-pairs,

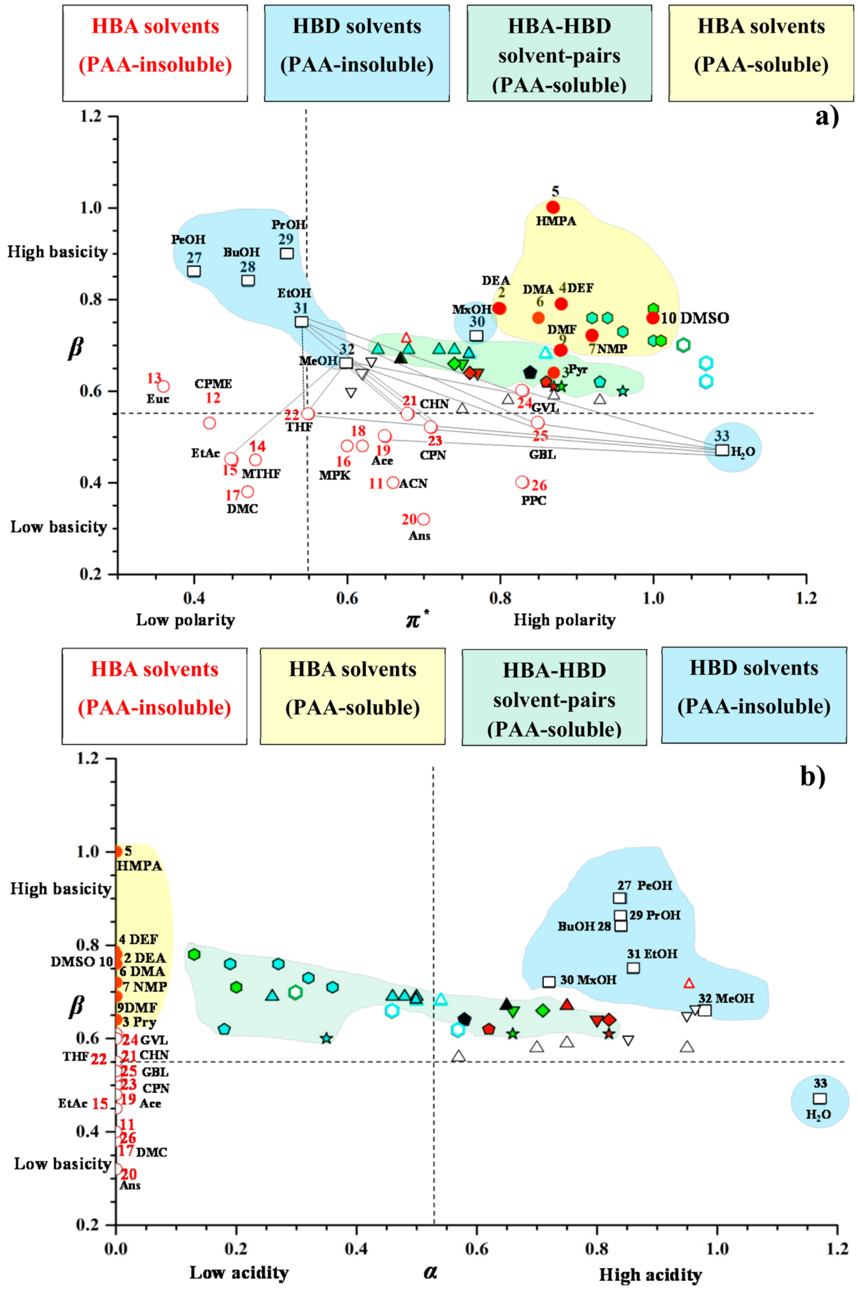

Figure 3. Kamlet−Taft solvatochromic parameters for pure solvents and solvent-pairs for (a) basicity (*β*) versus polarity (*π**) and (b) basicity (*β*) versus acidity (*α*). Blue-shaded regions show pure hydrogen bond donor (HBD) solvents that form heterogeneous PAA solutions (PAA-insoluble). Yellow-shaded regions show pure hydrogen bond acceptor (HBA) solvents that form homogeneous PAA solutions (PAA-soluble). Green-shaded regions show HBA−HBD solvent-pairs that form homogeneous PAA solutions (PAA-soluble). Red-numbered entries show HBA solvents that form heterogeneous PAA solutions (PAA-insoluble). Symbol and solvent lists are given in Figure 1 and in Tables S1 and S3 of the Supporting Information. Symbols with the same shape and same fill color are for different compositions of the solvent-pairs. Lines connecting some symbols denote HBA−HBD solvent-pairs considered for replacement of present (toxic) pure HBA solvents. Literature solvent-pairs for PAA-soluble are (red ▲) THF−MeOH, (black ▲) THF−EtOH, (teal ▲) THF−H_2O and literature solvent-pairs for PAA-insoluble are (red △) THF−MeOH (low HBA/HBD ratio), (teal △) THF−H_2O (low HBA/HBD ratio), (black Δ) ACN−H_2O. Replacement solvent-pairs for PAA-soluble are (red ▼) CHN−MeOH, (green ▼) CHN−EtOH, (red ◆) CPN−MeOH, (green ◆) CPN−EtOH, (red ⬠) GVL−MeOH, (teal ⬠) GVL−EtOH, (black ⬠) GVL−H_2O, (red ★) GBL−MeOH, (green ★) GBL−EtOH, (teal ★) GBL−H_2O, (teal ⬢) DMF−H_2O, (green ⬢) DMSO−H_2O and replacement solvent-pairs for PAA-insoluble are (▽) EtAc−MeOH, (teal ⬡) DMF−H_2O, (green ⬡) DMSO-H_2O.

and replacement solvent-pairs (Figure 1) were carried out using equimolar ratios of pyromellitic dianhydride (PMDA) and 4,4′-oxidianiline (ODA) at 25 °C. The crystalline solid of ODA monomer was first dissolved in the solvent or solvent mixture, and was stirred with a magnetic stirrer. The white powder of PMDA monomer was then added gradually into the ODA solution while stirring. After 3 h, the phase behavior of the PAA solution was observed. When homogeneous PAA solutions were formed, they were kept for 24 h with magnetic stirring to confirm the phase condition. In this work, soluble-PAA solution was defined as a homogeneous solution and insoluble-PAA solution was defined as a heterogeneous solution in which monomers or PAA did not dissolve completely in the solvent and exhibited phase separation. Sample photos of each solvent mixture are given in the Supporting Information (Figure S3).

Analysis of PAA. The functional groups of the polymer in the homogeneous PAA were analyzed by FT-IR, ^{1}H NMR, thermogravimetry (TGA), and gel permeation chromatography (GPC) and compared with commercial PAA solutions. Details are given in the following sections.

FT-IR Analysis. The homogeneous PAA solutions were cast onto a Teflon substrate and heated up to 80 °C in a vacuum oven for 16 h. The dried PAAs were mixed with potassium bromide tablets, and the samples were then dried at 60 °C in a vacuum oven for 2 h to remove moisture. The FT-IR spectra of the PAAs were measured in transmission mode with an FT-IR spectrometer (Jasco, FT/IR-230) with a resolution of 4 cm^{-1} and 512 scans.

^{1}H NMR Analysis. The homogeneous PAA solutions were cast onto a Teflon substrate and were then heated up to 70 °C in a vacuum oven for 1 h. The dried PAAs were dissolved in dimethyl sulfoxide-d_6. Tetramethylsilane (TMS) was used as internal standard. The ^{1}H NMR spectra of the PAAs were measured with ^{1}H NMR spectroscopy (Bruker, 500 MHz).

TGA Analysis. The homogeneous PAA solutions were cast onto a Teflon substrate and were then heated up to 80 °C in a vacuum oven for 16 h. Thermal stabilities of the dried PAA samples were estimated using a TG/DTA Instruments (Seiko Instrument Inc., model SII Exstat 6000) that was operated with a N_2 gas flow of 200 mL·min^{-1} and a heating rate of 10 °C·min^{-1} up to 800 °C.

GPC Analysis. Gel permeation chromatography (GPC) analyses were calibrated with polystyrene standards (PS) having molecular weights of 18.7, 50, 200, 400, and 900 kg·mol^{-1} as 0.5% (w/v) dimethylformamide (DMF) solutions. The PAA solutions for analysis were prepared as 0.5% (w/v) DMF solutions. All PAA samples and PS standard solutions were filtered through a 0.2 μm Teflon (Millex) before GPC measurements.

The GPC consisted of an HPLC pump (Jasco, Model PU 2080), a GPC column (Shodex, KD-804) and a UV/vis detector at a fixed wavelength (λ) of 270 nm (Jasco, Model 2070 Plus). The column was maintained at 40 °C, and the detector was kept at room temperature. DMF was used as the mobile phase with additives of 0.03 M lithium bromide (LiBr) and 0.06 M phosphoric acid (H_3PO_4). Mori et al.,[36] Haruki et al.,[37] and company literature[38] suggest that the addition of LiBr can suppress the polyelectrolyte effect that increases the intrinsic viscosity of highly dilute solutions and the addition of H_3PO_4 can recover residual PAA polymers from the column because it can reduce the interactions between the carboxylate group of PAA and the hydrophilic polymer gel stationary phase. The flow rate of the mobile phase was 1 mL·min^{-1} and the sample size was 20 μL.

RESULTS AND DISCUSSION

Results for preparation of homogeneous and heterogeneous poly(amic acid) (PAA) solutions for pure solvents, literature solvent-pairs, and identified replacement solvent-pairs are tabulated in Table S1 (Supporting Information) along with Hansen solubility (δ) parameters and Kamlet–Taft solvatochromic (K-T) parameters from the literature. The solubility parameter window for obtaining homogeneous PAA solutions (Figure 1) was evaluated by dissolution tests of PAA for 33 pure solvents and 17 solvent mixtures (ranging in 16.1–47.8 MPa$^{0.5}$) using data from Table S1 of the Supporting Information. The solubility parameter window was found to be 20.5–29.2 MPa$^{0.5}$ from dissolution tests for the monomers and literature estimations for the polymer.

After the first step of the methodology (Figure 2), the replacement solvent-pairs identified were tabulated in the second step. Replacement solvent-pairs are given by dashed lines in Figure 1 that connect a hydrogen bond acceptor (HBA) solvent with a hydrogen bond donor (HBD) solvent. It can be seen (Figure 1) that δ values of the replacement solvent-pairs have mixture solubility parameters that can cross the solubility parameter window according to changes of δ with composition.[14] Pure HBA solvents (Figure 1, (#1–10) and Table S1 of the Supporting Information) identified in the literature[2] allow preparation of homogeneous PAA solutions, but other pure HBA solvents, such as, cyclopentanone (CPN), γ-valerolactone (GVL), γ-butyrolactone (GBL) (Figure 1, (#23–25)) and pure HBD solvents, such as, pentanol, butanol, propanol, 2-methoxyethanol, and ethanol (EtOH) (Figure 1, (#27–31)) do not give homogeneous PAA solutions even though their δ values are within the solubility parameter window. Thus, the solubility parameter is unable to discriminate many cases of suitable solvents for preparing homogeneous PAA solutions as expected. Nevertheless, mixtures that fall outside of the solubility parameter window are likely to give unfavorable results and thus the solubility parameter window is an important indicator for solvent selection.

HBA solvents solvate PAA polymers via specific interactions with the polymer's carboxylate and amine groups.[39,40] The strength of the possible specific interaction of the solvent or solvent-pair mixture may be quantified with Kamlet–Taft solvatochromic (K-T) parameters,[30] π^* (polarity), β (electron donor), and α (electron acceptor) contributions.

Figure 3 shows a plot of K-T parameters for pure solvents, literature solvent-pairs, and replacement solvent-pairs using data from measurements in this work and the literature (Table S1 of the Supporting Information). Delineated regions (black-dashed lines) used for high and low basicity, high and low polarity, and high and low acidity were adopted from Jessop.[29] Homogeneous PAA-soluble solutions are obtained in pure HBA solvents (Figure 3, filled red circles) that have high polarity ($\pi^* > 0.87$) and high basicity ($\beta > 0.64$) as indicated by the yellow-shaded regions in Figure 3a,b, whereas pure HBD solvents (Figure 3, blue-shaded region) with low π^* values and pure HBA solvents with low β values do not form homogeneous reaction mixtures for PAA as shown by unfilled symbols in Figures 3. Lines in Figure 3 drawn between the symbols denote solvent-pair mixtures and are discussed later along with the green-shaded region and outliers.

To understand some of the reasons for the trend of the K-T parameters for HBA and HBD solvents shown in Figure 3, it is helpful to consider the reaction mechanism proposed by Volksen.[6] Volksen[6] reported that the dissolution behavior of PMDA in ODA solvent solutions begins with reaction at the PMDA particle solid–liquid interface. A gelatinous layer that contains PAA forms on the outside of the PMDA particle. As the thickness of the layer increases or swells with increasing reaction time, the size of the solid particle PMDA decreases. Finally, the PMDA monomer is consumed and the PAA gel is solvated so that a homogeneous PAA solution is obtained. Thus, the conditions for obtaining homogeneous PAA solutions are controlled by both kinetics and solvent-monomer, solvent–polymer interactions.

Ghosh et al.[8] reported that the reaction rate of PAA synthesis increased with increasing basicity of the solvents. Thus, it is likely that the reaction rate is controlled by solvent basicity which can be estimated by the K-T parameter, β. An HBA solvent having a high β value is required to form homogeneous PAA solutions. However, a number of pure HBA solvents are shown in Figure 3 (#12–26) that do not form the homogeneous solution with PAA and the reason can be thought of as not only being related to the kinetics of the PAA gel layer due to low β values, but also due to low solvent polarity (π^*). A solvent with high polarity is required to deactivate the carboxylate group in the gelatinous layer that promotes formation of poly(amic acid) (PAA).[41] Pure HBD solvents (Figure 3 and Table S1), such as, alcohols, do not have specific interactions with PAA so that heterogeneous PAA solutions are formed in spite of their high β values and their solubility parameter being within the solubility parameter window.

According to the K-T parameters shown for pure solvents in Figure 3, there are a wide range of α, β, and π^* values that could be used to prepare soluble-PAA solutions. Solvent mixtures can allow one to adjust solvent mixture acidity, basicity, and polarity characteristics. Lines shown in Figure 3a correspond to the solvent-pairs identified with the solubility parameter windows (Figure 1) according to the methodology of Figure 2 (step 2), but also include solvent-pairs proposed in the literature. Conditions of the experiments and the K-T parameters of solvent-pair mixtures measured in this work are given in the Supporting Information (Table S3). In Figure 3 and Table S3 of the Supporting Information, K-T parameters and PAA polymerization results for solvent-pairs proposed in the literature and for solvent-pairs proposed in this work are shown with filled symbols indicating that homogeneous (PAA-soluble) mixtures could be prepared.

Combination of an HBD solvent having high β and low π^* (e.g., methanol (MeOH) and ethanol (EtOH)) with an HBA solvent having low β and high π^* (e.g., tetrahydrofuran (THF)) allows preparation of homogeneous PAA solutions in confirmation with results reported in the literature.[17,20] Kamlet−Taft parameters for literature-proposed solvent-pairs were also studied in this work (Table S3 of the Supporting Information). According to results shown in Table S3 of the Supporting Information (THF−MeOH, THF−EtOH, and THF−H_2O), β and π^* values of the mixtures are sufficiently high to allow formation of homogeneous PAA solutions. However, for some conditions (low THF−H_2O ratio), even though β and π^* values are sufficiently high ($\beta > 0.64$, $\pi^* > 0.87$), phase separation occurs because solvent conditions move close to or outside of the solubility parameter window (Figure 1) and local composition effects probably exist.[49]

The K-T parameters for all replacement solvent-pair mixtures are shown in Table S3 of the Supporting Information along with conditions and results. Results are also shown in Figure 3 in the green-shaded region. Other solvent-pairs (DMF−H_2O and DMSO−H_2O) are shown for discussion.

According to step 4 of the methodology (Figure 2), measuring the K-T parameters for the solvent-pair mixture allows one to assess whether the solution properties in terms of β and π^* parameters (Figure 3a) will move toward the PAA-soluble region of the pure solvents (yellow-shaded area). The approximate increase or decrease of the K-T parameters for the solvent mixtures over their mole fraction average can be seen by the ΔK-T values shown in Table S3 of the Supporting Information. It is desirable to increase both β and π^* values for a given solvent-pair mixture by combining HBA solvents that have high π^* and low β values and HBD solvents that have high β and low π^* values The formation of complex molecular species between HBA and HBD solvents may also have a synergistic effect,[42−44] which enhances the K-T parameters of the solvent mixtures. A clear advantage of using HBA−HBD solvent-pair combinations is the synergism in K-T parameters that can result possibly due to local composition effects.

The results of preparations of PAA solutions of the replacement solvent-pairs proposed in this work (Table S3 of the Supporting Information) show that homogeneous PAA solutions could be prepared for all solvent-pairs, except for ethyl acetate (EtAc)−MeOH mixtures. According to Figure 3, the preparation of homogeneous PAA solutions requires a solvent having high $\pi^*$and β parameters relative to the pure HBA solvents PAA-soluble region (Figure 3a). Suitable solvent-pairs are a combination of an HBD solvent having high β and low π^* values (e.g., MeOH and EtOH) with an HBA solvent having low β and high π^* values (e.g., CPN, GVL, and GBL) both relative to the yellow region (Figure 3a) for which β and π^* parameters (green-shaded region in Figure 3a) of the replacement solvent-pairs show an increase toward the pure HBA solvents PAA-soluble region (Figure 3a). For the case of EtAc−MeOH mixtures (▽ three mixture points), however, it is likely that homogeneous PAA solutions could not be obtained due to low solvent polarity (Figure 3a) and high acidity (Figure 3b) of the solvent mixtures relative to the pure HBA solvents PAA-soluble region (Figure 3a). The minimum $\pi^*$and β values required for preparing homogeneous PAA solutions in nonaqueous solvent mixtures were determined to be 0.67 and 0.61, respectively, whereas the minimum $\pi^*$and β values required for aqueous solvent mixtures were determined to be 0.68 and 0.59, respectively.

The δ values of the literature and replacement solvent-pairs for preparing the homogeneous PAA solutions shown in Table S3 of the Supporting Information were within the solubility parameter window (Figure 1). On the other hand, the δ values of DMF-H_2O and DMSO-H_2O solvent-pairs (Table S1 of the Supporting Information) that are close to or outside of the solubility parameter window cannot be used to prepare the homogeneous PAA solutions, even though their $\pi^*$and β values are sufficiently high for aqueous solvent mixtures ($\pi^* > 0.68$ and $\beta > 0.59$). Thus, the solubility parameter is also important in the selection of solvent-pair mixtures for preparing homogeneous PAA solutions.

Local composition of solvent mixtures[49] around polymer and monomers also play an important role for preparing homogeneous PAA solutions. Although δ value of THF−MeOH at weight ratio 4/6 (Table S3 of the Supporting Information) are within the solubility parameter window (Figure 1) and its $\pi^*$and β parameters are high enough for nonaqueous solvent mixtures ($\pi^* > 0.67$ and $\beta > 0.61$), homogeneous PAA solutions are unable to be obtained in THF−MeOH at a weight ratio 4/6 (Table S3 of the Supporting Information). Solvent mixture ratios of the literature and replacement solvent-pairs for preparing homogeneous PAA solutions (Table S3 of the Supporting Information) are HBA-rich compositions. For the case of pure solvents Figure 1, (#1−10) and Table S1 of the Supporting Information), only those having HBA characteristics can be used to prepare homogeneous PAA solutions. Thus, the monomers and PAA are preferably solvated in an HBA solvent rather than an HBD solvent although local composition effects also exist.

Results in Table S3 of the Supporting Information show that solvent-pairs with suitable composition ratios can be used to prepare homogeneous solutions, whereas the pure solvents of the solvent-pairs are unable to form homogeneous solutions. Results in Table S3 of the Supporting Information emphasize the advantages of using HBA−HBD solvent-pairs to adjust values of both the solubility parameter and K-T parameters of the mixture.

Analysis of PAA Characteristics. Appearances of the synthesized PAA in the replacement solvent-pair mixtures were similar or identical to commercial PAA solution (Figure S3 of the Supporting Information). The functional groups and thermal stability of polymers formed were analyzed by FT-IR (Figure S4 of the Supporting Information), ^{1}H NMR (Figure S5 of the Supporting Information), and TGA (Figure S6 of the Supporting Information) methods confirming that PAA had been synthesized for the solvent-pairs shown in Table 1 and that their characteristic and properties were similar to those of commercial PAA solutions.

Table 1. Properties of Poly(amic acid) (PAA) Precursor Solutions Formed with Solvent-Pair Mixtures Identified in This Work and Those Reported in the Literature[a]

Replacement solvent-pairs	$\overline{M}_w$ 10^5 g/mol	PDI ($\overline{M}_w/\overline{M}_n$)	DP ($\overline{M}_n/\overline{M}_o$)	Ref.
▼CHN-MeOH	0.34	1.55	52.4	This work
▼CHN-EtOH	0.67	1.52	104.8	This work
◆CPN-MeOH	0.39	1.55	59.7	This work
◆CPN-EtOH	0.93	1.47	151.3	This work
⬟GVL-MeOH	1.11	1.48	180.0	This work
⬟GVL-EtOH	1.32	1.54	204.5	This work
⬟GVL-H_2O	1.47	1.59	222.0	This work
★GBL-MeOH	1.11	1.48	178.2	This work
★GBL-EtOH	1.19	1.54	185.2	This work
★GBL-H_2O	1.43	1.56	218.4	This work
Literature solvent-pairs				
▲THF-MeOH	1.91	2.51	181.9	[18]
▲THF-MeOH	3.03	-	-	[20]
▲THF-EtOH	4.50	-	-	[20]
△THF-H_2O	4.01	-	-	[20]
Other solvents and solvent pairs				
CO_2+DMF	0.10	3.5	7.3	[37]
⬢DMA	4.20	-	-	[20]
■NMP	3.80	-	-	[20]
■ Commercial PAA in NMP	1.69	1.49	271.1	This work

[a] PDI = polydispersity index ($\overline{M}_w/\overline{M}_n$). DP = degree of polymerization ($\overline{M}_n/\overline{M}_o$). $\overline{M}_o$ = molecular weight of repeating unit of PAA, 418 g/mol.

The molecular weights ($\overline{M}_w$) of PAAs in the replacement solvent-pairs were lower than from those in the literature solvent-pairs (Table 1), which can be attributed to optimization of conditions, such as, temperature, concentration, solvent-pair mixture concentration, mixing, and technological factors. However, the molecular weights ($\overline{M}_w$) of the PAAs, their polydispersity index (PDI), and their degree of polymerization (DP) for many of the replacement solvent-pairs were comparable with those of commercial PAA solution. Considering the dependence of the $\overline{M}_w$ on the K-T parameters (Figure S7 of the Supporting Information), the molecular weights of PAA tended to increase with increasing solvent mixture polarity (π^*) probably due to stronger deactivation of the carboxylate group caused by the solvent polarity. However, in a solvent mixture, local composition probably plays an important role in the polymerization. Comparing the molecular weights of PAA among the replacement solvent-pairs, the preparation of homogeneous PAA solutions in GVL−H_2O mixture gave the highest molecular weight with the narrowest molecular distribution in terms of the polymer PDI.

There are several factors that affect the molecular weight of PAA formed. When the solvent-pair mixture contains a nonpolar solvent, such as CO_2, precipitation occurs as shown for DMF-CO_2 (Table 1) as reported in the literature.[37] For some of the replacement solvent-pair mixtures, differences in $\overline{M}_w$ can be attributed to side reactions that occur between PAA and the solvent-pairs (CHN−MeOH, CHN−EtOH, CPN−MeOH, CPN−EtOH, Table 1), such as, hemiketal formation.[45,46] The color of the PAA solutions in these solvent mixtures changed from yellow to dark brown (Figure S3 of the Supporting Information) and precipitation occurred after 24 h.

Other Renewable-Solvent Systems. For seeking new renewable-HBA solvents, dihydrolevoglucosenone (cyrene) has been recently proposed[47] and it can be expected to be useful due to its high π^* (0.92), high β (0.61), low α (0) values. Cyrene combined with MeOH, EtOH, or H_2O HBD solvents could possibly be used for preparing homogeneous PAA solutions due to favorable Kamlet−Taft solvatochromic parameter values and its solubility parameter (22.7 MPa$^{0.5}$) being within the solubility parameter window of the target monomers and polymer studied in this work.

Temperature has not been considered in this work, but has a large effect on dissolution, solvent interactions, reaction rate, solubility parameter and Kamlet−Taft solvatochromic parameters. For example, polyimide could be synthesized by using high temperature water at 180 °C.[48] The present methodology is based on solvent preparation at 25 °C.

■ CONCLUSIONS

A methodology for selecting safe and renewable solvent-pair mixtures for preparing homogeneous polymer precursor solutions commonly used in engineering plastics has been developed. The proposed methodology uses a chemical safety index, the Hansen solubility parameter (δ) and Kamlet−Taft solvatochromic parameters to select solvent-pairs that have hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) properties. Renewable solvent-pairs that have HBA and HBD properties are chosen to obtain favorable Kamlet−Taft solvatochromic parameters for preparing homogeneous polymer precursor solutions.

In combining HBA and HBD solvent-pairs for producing soluble poly(amic acid) solutions, minimum values of $\pi^*$and β parameters should be at least 0.67 and 0.61, respectively, for nonaqueous solvent mixtures and at least 0.68 and 0.59, respectively, for aqueous solvent mixtures. Local composition most likely also plays a role in the suitability of the solvent-pair mixture. Of the replacement solvent-pair mixtures, γ-valerolactone−EtOH, γ-valerolactone−water, and γ-butyrolactone−water provided polymer precursor solutions that were comparable with commercial formulations that use *N*-methyl-2-pyrrolidone. Additional solvent-pairs for homogeneous polymer precursor solutions can be identified through the use of the methodology presented in this work. Further, the methodology presented in this work can be used to study the preparation of other engineering plastics polymer precursor solutions with safe and renewable solvent-pair combinations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental results of preparing poly(amic acid) (PAA) solutions with solvent and solvent-pairs along with solubility parameter (δ) and Kamlet−Taft solvatochromic (K-T) parameters; indicator relationships used to determine Kamlet−Taft solvatochromic parameters; experimental results for preparation of homogeneous and heterogeneous poly(amic acid) (PAA) solutions of 5 wt % in literature and replacement hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) solvent-pairs at 25 °C; solubility parameter group contribution method used for pyromellitic dianhydride (PMDA), 4,4′-oxydianiline (ODA), and poly(amic acid); correspondence of FT-IR wavenumber and functional groups, differential thermogravimetric analysis (DTGA) temperature of poly(amic acid) (PAA) in the replacement solvent-pairs; chemical structures of pyromellitic dianhydride (PMDA), 4,4′-oxydianiline (ODA), poly(amic acid) (PAA); molecular structures of solvatochromic indicators used in this work; solution appearance of homogeneous and heterogeneous poly(amic acid) (PAA) solutions; FT-IR spectra of poly(amic acid) (PAA) synthesized in the replacement solvent-pairs; ^{1}H-NMR spectra of poly(amic acid) (PAA) synthesized in the replacement solvent-pairs; TGA results of poly(amic acid) (PAA); molecular weight ($\bar{M}_w$) of poly(amic acid) (PAA) as a function of solvent or solvent mixture; gel permeation chromatography results for poly(amic acid) (PAA) synthesized in the replacement solvent-pairs. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00474.

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Notes

The authors declare no competing financial interest.

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