# Synthesis of Aliphatic-Aromatic Polyimides by Two-Step Polymerization of Aliphatic Dianhydride and Aromatic Diamine

JONG-YOUNG JEON* and TAE-MOON TAK

Department of Natural Fiber Sciences, Seoul National University, Seoul, Korea

## SYNOPSIS

Aliphatic-aromatic polyimides were synthesized by polycondensation reaction in solvent. The effects of variables such as the kind of solvent, reaction time and temperature, and monomer concentration were investigated in detail on the reaction of 1,2,3,4-butanetetra-carboxylic dianhydride and 4,4'-oxydianiline or 4,4'-diaminodiphenylmethane. The viscosities of polyimides were between 0.22 and 0.46 dL/g. The polyimides were soluble in some aprotic polar solvents, such as $N,N'$-dimethylacetamide (DMAc), $N$-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), and $N,N'$-dimethylformamide (DMF). They began to decompose at 380–410°C in air, and 10% weight loss temperatures were 430–450°C. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The typical method for the synthesis of polyimide is the two-step polycondensation of a dianhydride with a diamine in aprotic polar solvents[1-3] such as $N,N'$-dimethylacetamide (DMAc) and $N$-methyl-2-pyrrolidone (NMP). A polyamic acid as polyimide precursor is obtained in the first step; then cyclo-dehydration of this precursor polymer, either by thermal or chemical treatment, yields the polyimide. Polyimides derived from an aromatic dianhydride and an aromatic diamine are high-performance materials because of their outstanding properties, including thermal and chemical stability. However, they are difficult to fabricate, owing to their insolubility and their high glass transition temperature. Recently, several polyimides that are soluble in organic solvents have been reported.[4,5] Some articles[5,6] have discussed the structure–solubility relationships in organic soluble and thermal stable polyimides.

This article describes the synthesis and characterization of aliphatic-aromatic polyimides that were prepared from an aliphatic dianhydride and an aromatic diamine monomer.

## EXPERIMENTAL

### Reagents

1,2,3,4-Butanetetracarboxylic dianhydride (BTDA) was prepared by dehydration of 1,2,3,4-butanetetracarboxylic acid (BTCA, Aldrich Chemical Co.). Prepared BTDA was recrystallized from 4-methyl-2-pentanone before use. 4,4'-Oxydianiline (ODA, Aldrich Chemical Co.) and 4,4'-diaminodiphenylmethane (DADM, Aldrich Chemical Co.) were recrystallized from ethanol. $N,N'$-Dimethylacetamide (DMAc), $N$-methyl-2-pyrrolidone (NMP), and $N,N'$-dimethylformamide (DMF) were obtained from Aldrich Chemical Co. All the solvents were dried by using calcium hydrate and distilled before being stored in 4 Å molecular sieves. Other laboratory grade reagents were used without further purification. Among them were acetic anhydride, benzene, 4-methyl-2-pentanone, pyridine, and calcium hydrate.

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**Figure 1**    NMR spectra of BTCA and BTDA.
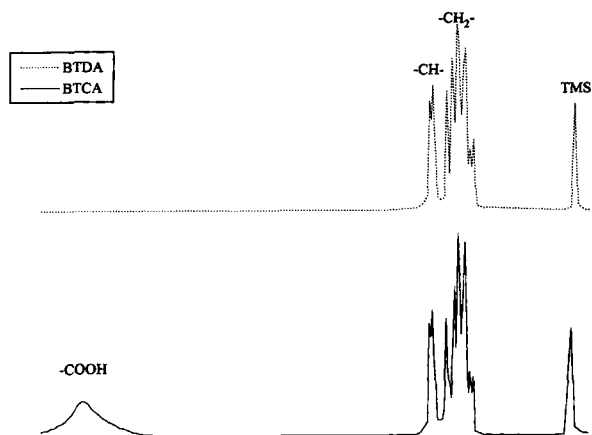


**Figure 2**    NMR spectra of BTDA/DADM polyamic acid and corresponding polyimide.

## Measurement

The viscosity of polyamic acid solution was measured by a ubbelohde viscometer at a concentration of 0.5 g/dL in DMAc at 30°C. $^1$H-NMR spectrum was obtained from a Bruker AM 100 spectrometer. Elemental analysis was performed using a Carlo Erba MOD 1106. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were run on a DuPont model 951. Differential scanning calorimetry (DSC, DuPont 1090) was used for evaluation of thermal behavior in air atmosphere. Molecular weight distribution was obtained from gel-permeation chromatography (GPC) on a Waters model 150C. In order to judge solvent effects such as dissolution, swelling, and insolution, samples of polyimide were placed in various solvents and allowed to stand for 7 days. The solubility parameter of polymer could be calculated by the second-hand method.[7]

## Preparation of BTDA from BTCA

BTCA was placed in a flask with a 2 mol excess of acetic anhydride, the mixture was refluxed for 4 h, and acetic acid yielded was distilled from the mix-

ture. The hot mixture was poured into a crystallizing dish to precipitate BTDA. The BTDA was collected by filtration and washed several times with 4-methyl-2-pentanone to free acetic anhydride. Before polymerization, BTDA was dissolved in hot 4-methyl-2-pentanone, filtered, and then vacuum dried at 80°C.

NMR showed 2.0–3.0 ppm ($R_2CH$ — $H$) and 2.5–3.0 ppm ($R_3$ — $C$ — $H$).

ANAL. Calcd. for $C_8H_6O_6$, (%): C, 48.28, H, 2.98, O, 48.74. Found: C, 48.48, H, 3.05, O, 48.47.

## Synthesis of Polyimide

A four-necked 250 mL flask was equipped with a seal teflon stirrer, nitrogen gas inlet tube, reflux condenser with $CaCl_2$ guard tube, and thermometer,

**Table I    Elemental Analysis of BTCA and BTDA**

|  | Molecular Formula |  | Elemental Analysis | | |
|---|---|---|---|---|---|
|  |  |  | C | H | O |
| BTCA | $C_8H_{10}O_8$ | Calcd. | 39.75 | 4.91 | 55.66 |
|  |  | Found | 41.03 | 4.30 | 54.66 |
| BTDA | $C_8H_6O_6$ | Calcd. | 48.28 | 2.98 | 48.74 |
|  |  | Found | 48.48 | 3.05 | 48.47 |

**Table II    Effect of Solvent on the Viscosity and Yield of Polyamic Acid[a]**

| Polyamic Acid | Solvent | Viscosity $(dL/g)^b$ | Yield (%) |
|---|---|---|---|
| BTDA/ODA | DMAc | 0.43 | 90 |
|  | NMP | 0.41 | 90 |
|  | DMF | 0.30 | 90 |
| BTDA/DADM | DMAc | 0.40 | 90 |
|  | NMP | 0.36 | 90 |
|  | DMF | 0.35 | 90 |

[a] Polymerization was carried out with 10 wt % of monomers concentration at 20°C for 7 h.
[b] Measured at content of 0.5 g/dL polyamic acid in DMAc at 30°C.

**Table III  Effect of Monomer Concentration on the Viscosity and Yield of Polyamic Acid[a]**

| Polyamic Acid | Concentration (wt %) | Viscosity (dL/g)[b] | Yield (%) |
|---|---|---|---|
| BTDA/ODA | 5 | 0.20 | 85 |
| | 10 | 0.43 | 90 |
| | 15 | 0.37 | 90 |
| | 20 | 0.22 | 90 |
| BTDA/DADM | 5 | 0.17 | 85 |
| | 10 | 0.40 | 90 |
| | 15 | 0.37 | 90 |
| | 20 | 0.30 | 90 |

[a] Polymerization was carried out in DMAc at 20°C for 7 h.

[b] Measured at content of 0.5 g/dL polyamic acid in DMAc at 30°C.

respectively. The equimol BTDA was slowly added to the flask containing a diamine and solvent. The reaction mixture was kept at temperature with vigorous stirring to yield polyamic acid with high molecular weight. When the viscosity was no longer increased, the polyamic acid solution was cast onto the glass plate. The major amount of solvent was removed and dried in an oven at 70°C for 2 h. The resulting film partially dried could be peeled from
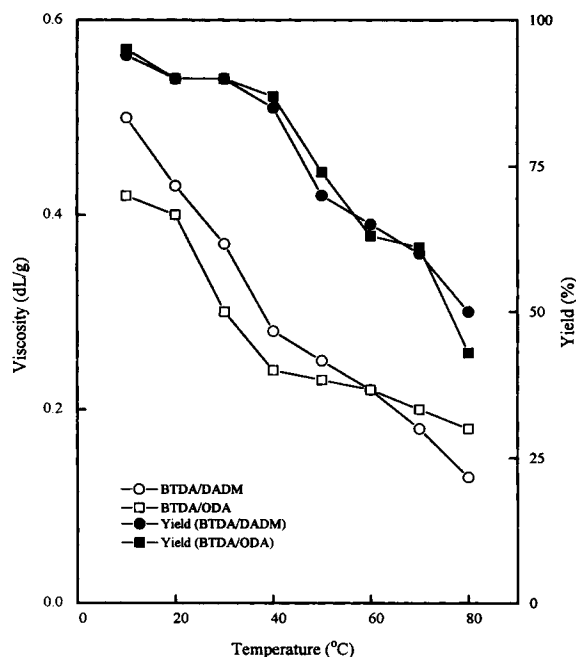


**Figure 4**  The viscosity of polyamic acids against reaction time. 1) Polymerization was carried out with 10 wt % of monomers concentration at 20°C in DMAc.

the glass plate and then clamped to the steel frame. Next, the film was cyclo-dehydrated by the thermal and/or chemical method.

NMR of polyamic acid showed 2.0–3.0 ppm $(R_2CH-H)$ and 2.5–3.0 ppm $(R_3-C-H)$, 3.0–



**Figure 3**  Effect of the reaction temperature on the viscosity and yield of polyamic acids. 1) Polymerization was carried out with 10 wt % of monomers concentration in DMAc for 7 h.
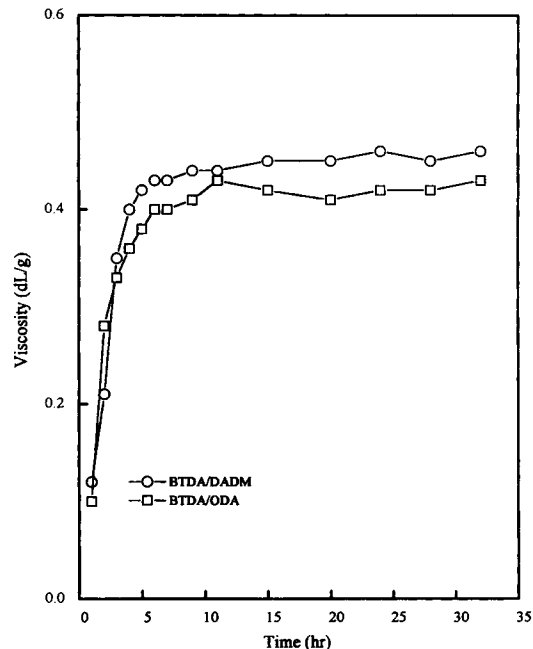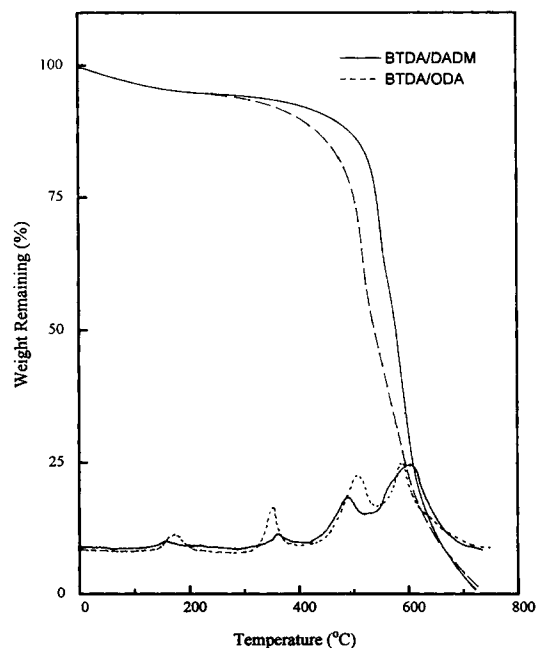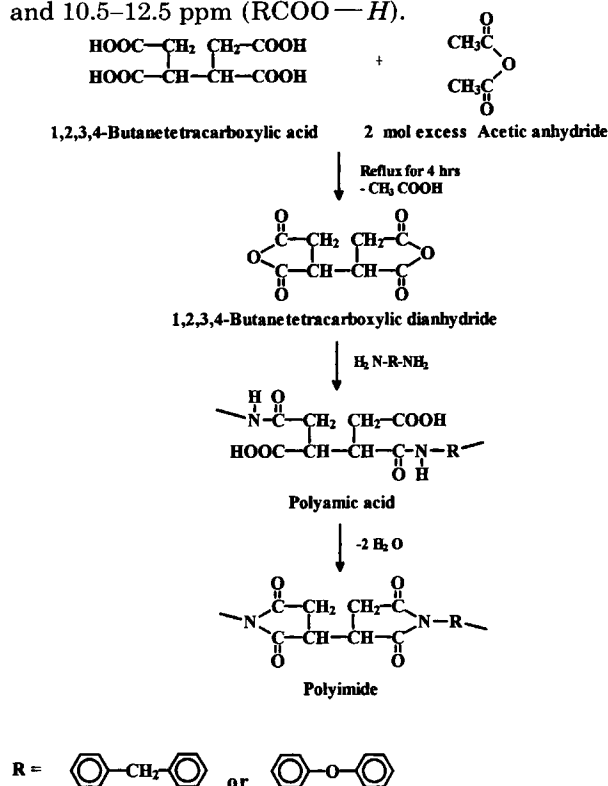


**Figure 5**  TGA and DTG traces of polyimides.

4.0 ppm (Ar$_2$—CH—$H$), 5.0-8.0 ppm (RCON-$H$), and 10.5-12.5 ppm (RCOO—$H$).



1,2,3,4-Butanetetracarboxylic acid        2 mol excess Acetic anhydride

Reflux for 4 hrs
- CH$_3$COOH

1,2,3,4-Butanetetracarboxylic dianhydride

H$_2$N-R-NH$_2$

Polyamic acid

-2 H$_2$O

Polyimide

R = or

## RESULTS AND DISCUSSION

Figure 1 is the NMR spectra of BTCA and BTDA. In both spectra, the absorption peaks of alkane protons were observed at 2.0-3.0 ppm (R$_2$—CH—$H$) and 2.5-3.5 ppm (R$_3$—C—$H$), respectively. The characteristic peak of carboxylic acid, however, at 10.5-12.5 ppm was only detected in BTCA spectrum. The peak area ratio of the alkane protons absorption peaks in BTDA is nearly the same as the theoretical. This means that the alkane protons are not influenced by the dehydrating agent, acetic anhydride, during the dehydrating reaction of BTCA. Table I represents the elemental analysis of BTCA and BTDA. They yielded the same result as the NMR spectra. It was found that BTCA may be completely converted into BTDA.

Figure 2 shows the NMR spectra of BTDA/DADM polyamic acid and corresponding polyimide. In the spectra, the absorption peaks of alkane and aromatic ring protons were observed at 2.0-3.0 ppm (R$_2$—CH—$H$), 2.5-3.5 ppm (R$_3$—C—$H$), 3.5-4.0 ppm (Ar$_2$—CH—$H$), and 7.0-8.5 ppm (Ar—$H$), respectively, but the absorption peak of primary amine (R—NH—$H$), belonging to the diamine monomer, was not detected at 1.0-5.0 ppm.

The characteristic peaks of amic acid owing to the residual carboxylic acid (RCOO—$H$) and secondary amine protons (—CON$H$—) were only detected in the amic acid spectrum. It can be deduced from those spectra that the product obtained at the first step is probably polyamic acid, and the final product consisted mostly of imide.

Table II represents viscosity and yield of polyamic acid yielded from various solvents. The viscosity of polymer obtained in DMAc was larger than that yielded in other solvents. The solvent effect on the molecular weight of the polyamic acid has been observed in several condensation reactions.[1,8–10] The result may be related to the change of reactivity of reagents and the formation of a solvent-propagating species complex. The propagating reaction occurs at the carbonyl carbon atoms of anhydride proton by the unshared electron pair of nitrogen atom of amine. The nucleophilicity of amine is significantly influenced by the solvent basicity.[10] Solvent being sufficiently polar acts as a Lewis base to anhydride reagents and increases the nucleophilicity of the dissolved diamine. Polar solvents should form strong hydrogen bonds with the free carboxylic groups and the amides belonging to the precursor.[11] They are formed between the electronagative atom of solvent and potentially positive-charged hydrogen atom of —OH and —NH— of amic acid. The basicity of solvents increase DMF < NMP < DMAc.[10]

Table III shows the effect of monomer concentration on the viscosity and yield of the polyamic acid. The viscosity increased with increasing reactant content up to 10 wt %; however, above that concentration it decreased gradually with increasing concentration. The result can be explained that in the case of the low content, the probability of impingements on each other is low for the propagation
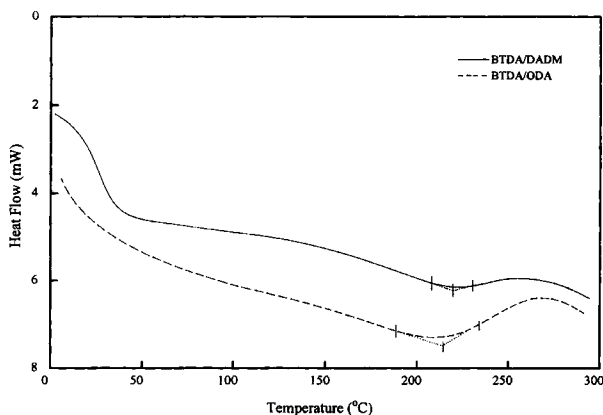


**Figure 6** DSC thermograms of polyimides.

reaction. On the other hand, both the probability of impingements and the amount of exothermic heat increased with increasing content of the reagent. The generated heat probably disturb the propagating reaction owing to exothermic reaction.

Figure 3 shows the effect of the reaction temperature. The viscosity of polyamic acid became diminished in proportion to the increasing temperature. When the reaction was performed above 40°C, it was probably difficult to give off the heat generating this reaction, probably because the reaction of dianhydride and diamine is a vigorously exothermic reaction.[1,3] Generally, the synthesis of polyimides are performed in the temperature range of 15–75°C;[3] above 75°C, the molecular weight becomes markedly decreased; above 100°C, cyclization into imide ring occurs during synthesis of polyamic acid; above 150°C, the cyclization is very rapid. If the cyclization into imide ring occurs before polyamic acid grows to maturity, the propagating reaction does not proceed. Therefore, the reactions should be performed below 70°C.

Figure 4 explains the result of polymerization with various reaction times. The viscosity of polymers gradually increased until a reaction time of 15 h. But after that time, it is maintained. From this result, the propagating reaction gradually proceeded
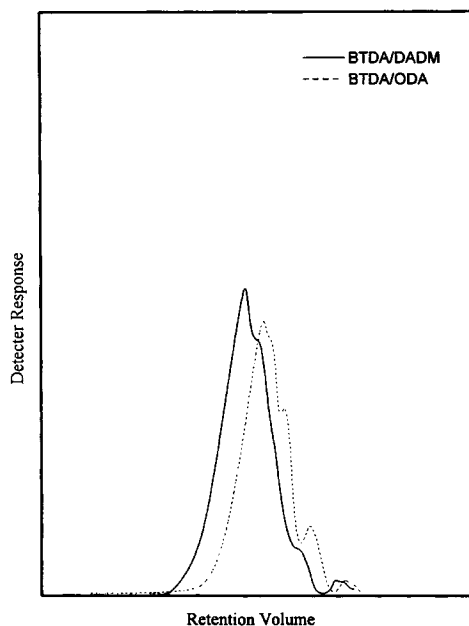


Figure 7 GPC chromatograms of the polyimides.

with the reaction time to reach a limited viscosity value; after that state, the reaction did not proceed.

The TGA curves of BTDA/DADM and BTDA/ODA polyimides are shown in Figure 5. Thermo-

Table IV    Solubility of BTDA/ODA and BTDA/DADM Polyimide[a]

| No. | Solvent | $\delta_d$ | $\delta_p$ | $\delta_h$ | $\delta_t$ | Solubility |
|-----|---------|-----|-----|-----|-----|-----------|
| 1 | Acetic acid | 7.1 | 3.9 | 6.6 | 10.5 | IS |
| 2 | Acetic anhydride | 7.8 | 5.7 | 5.0 | 10.9 | IS |
| 3 | 1-Butanol | 7.8 | 2.8 | 7.7 | 11.3 | IS |
| 4 | Chloroform | 8.7 | 1.5 | 2.8 | 9.3 | IS |
| 5 | m-Cresol | 8.8 | 2.5 | 6.3 | 11.1 | S |
| 6 | N,N-Dimethylacetamide | 8.2 | 5.6 | 5.0 | 11.1 | S |
| 7 | N,N-Dimethylformamide | 8.5 | 6.7 | 5.5 | 12.1 | S |
| 8 | Dimethyl sulfoxide | 9.0 | 8.0 | 5.0 | 13.0 | S |
| 9 | 1,4-Dioxane | 9.3 | 0.9 | 3.6 | 10.0 | IS |
| 10 | Ethanol | 7.7 | 4.3 | 9.5 | 13.0 | IS |
| 11 | Formamide | 8.4 | 12.8 | 9.3 | 17.9 | IS |
| 12 | Formic acid | 7.0 | 5.8 | 8.1 | 12.2 | SW |
| 13 | Glycerol | 8.5 | 5.9 | 14.3 | 17.6 | IS |
| 14 | Methanol | 7.4 | 6.0 | 10.9 | 14.5 | IS |
| 15 | N-Methyl-2-pyrrolidone | 8.8 | 6.0 | 3.5 | 11.2 | S |
| 16 | Nitrobenzene | 9.8 | 4.2 | 2.0 | 10.9 | S |
| 17 | 1-Propanol | 7.8 | 3.3 | 8.5 | 12.0 | IS |
| 18 | Pyridine | 9.3 | 4.3 | 2.9 | 10.7 | SW |
| 19 | Tetrahydrofuran | 8.2 | 2.8 | 3.9 | 9.5 | IS |
| 20 | Toluene | 8.8 | 0.7 | 1.0 | 9.1 | IS |

[a] Besides continuously at 25°C for 7 days, when the sample was partial soluble in solvent, the sample was heated at 70°C for 24 h.

Where S is soluble, SW is swell, and IS is insoluble in solvent.

grams were obtained by heating the samples in air at a heating rate of 20°C/min. Both polyimides were nearly the same pattern according to TGA. The rate of weight loss was confirmed in DTG (Fig. 5). A weight loss of 5% up to 150°C in all polymers may be attributed to the absorbed moisture. Initial decomposition temperature for these polymers was in the range of 300–350°C, where the major weight loss was observed in the range of 550–600°C. DSC traces of polyimides are given in Figure 6. All the polyimides showed a endothermic transition in the range of 100–170°C, which may be due to loss of absorbed moisture. An endothermic peak at 235–240°C is due to glass transition of these polymers.

The typical solubility of polymers is listed in Table IV. These aliphatic-aromatic polyimides had good solubility in several aprotic polar solvents such as DMAc, NMP, DMF, and DMSO, but with poor solubility in other organic solvents. Solubility parameter composed of dispersion ($\gamma$), polar ($\gamma_p$), and hydrogen bonding ($\gamma_h$) force was represented with a weak polar and weak hydrogen force. Of various approaches that attempted to improve their solubility,[6,12] introduction of aliphatic linkages in the polymer backbone met with some success. In the present work, these polyimides improved their solubility. This improved solubility is advantageous to the processability of polymers.

Figure 7 shows GPC curves of polyimides. The molecular weight distribution of polyimides lay in the range of 1.5–2.5.

## CONCLUSION

The aliphatic dianhydride, namely BTDA, was prepared by cyclodehydration of BTCA. The aliphatic-aromatic polyimides were synthesized by the polycondensation of aliphatic dianhydride (BTDA) and aromatic diamine, and characterized by NMR, DSC, TGA, GPC, and solubility. These polyimides had good solublity in aprotic polar solvents such as DMAc, NMP, DMF, and DMSO, and could be cast into films. These polyimides showed good thermal stability. Introduction of aliphatic linkages improves the solubility; however, the molecular weight of the polyimides was not sufficient enough. Greater improvements of polymerization methods and structural modifications are needed for increased molecular weight and complete solubility.

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