# Cyclic ureas as solvents for poly(aryl ether) synthesis

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## Summary

The synthesis of various poly(aryl ethers) and related small molecule compounds were examined using the cyclic urea 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (N,N′-dimethylpropylene urea, DMPU) as the solvent. The results showed that generally higher molecular weight or yields were obtained under less stringent conditions, as compared to other common polymerization solvents. The enhancement was most notable for polymerizations involving aryl fluorides with a lower reactivity than conventionally activated dihalide monomers, e.g. ketones, sulfones. Poly(aryl ethers) displayed excellent solubility in DMPU, which was beneficial in the cases where more rigid heterocyclic-aryl ether polymers are formed.

## Introduction

Nucleophilic aromatic substitution of activated halides by phenoxides is a well established polymerization reaction for the synthesis of poly(aryl ethers) (1-3). The polymerizations require the use of dipolar aprotic solvents, e.g. N-methylpyrrolidone (NMP), dimethyl acetamide (DMAC) or dimethyl sulfoxide (DMSO). Miller has reported that the dramatically enhanced reaction rates observed with dipolar aprotic solvents is, in part, due to good cation solvation, affording a more nucleophilic phenoxide anion (4). This suggests a more coordinative dipolar aprotic solvent may be a better reaction solvent for nucleophilic aromatic substitution. For instance, Hexamethylphosphoramide (HMPA) is known to be highly coordinative and is useful for the generation of free anions (5). However, due to the carcinogenic nature of HMPA it should be avoided (6), which has led to the development of several alternatives. Most notably, the cyclic urea, 1,3-Dimethyl-3,4,5,6-tetra- hydro-2(1H)-pyrimidinone (N,N′-dimethylpropylene urea, DMPU), was shown to be an excellent replacement solvent for HMPA, affording similar results in a variety of reactions (7). In addition to being highly coordinative, DMPU is also
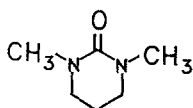


DMPU

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an excellent polymer solvent which could be beneficial in polymerizations where more rigid heterocyclic-aryl ether polymers are formed. In this paper, we will describe some of our results regarding the use of DMPU to exemplify the utility of this solvent for poly(aryl ether) synthesis.

## Experimental

The 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone was vacuum distilled prior to use from calcium hydride. The polymerizations were carried out by conventional methods, utilizing either a toluene azeotrope (8). More detailed procedures for the synthesis of the poly(perfluoroalkylene aryl ethers) (9), poly(1,2,4-triazole aryl ethers) (10), 1,2,4-triazole derived diamines (11), poly(aryl ether phenylquinoxalines) (12), poly(aryl ether benzazoles) from A-B monomers (13), and poly(aryl ethers) via sulfonate displacement (14) are published elsewhere. Intrinsic Viscosity measurements were made using a Cannon-Ubbelhohde viscometer and were determined by the single point method. The solvent used for intrinsic viscosity measurements was NMP except in the case of polymers 4a-c and 12b, where chloroform and DMPU were used, respectively.

## Results and Discussion

Our first results suggesting the acceleration of nucleophilic aromatic substitution in DMPU involved fluoro-displacements with 2-fluoro-1-perfluorooctylbenzene (1) (9) (Scheme I). Table 1 gives the results for the reaction of 1 with m-cresol using potassium carbonate as the base in DMPU as well as several amide solvents. In NMP, the ether product (2) was formed in only 70 % yield after 20 h at 170 °C. This is in contrast to displacements involving the analogous 4-isomer, which occurred quantitatively under these conditions. The reaction of 1 in DMPU was found to give a significantly better yield as compared to the amide solvents, i.e. 90 %, as did a 2:1 NMP:DMPU mixture. Copolymerizations of 2,4-difluoro-1-perfluorooctylbenzene (3) with 4,4'-difluorobenzophenone and bisphenol-AF were carried out in an NMP:DMPU solvent system using the following stepwise procedure. Monomer 3 was allowed to react with an excess of bisphenoxide to quantitatively displace the 2-fluoro group. This was followed by the addition of a more reactive aryl dihalide to complete the polymerization (Scheme II). By using an NMP:DMPU solvent mixture high conversion was attained in the first step, while maintaining good solubility for the more highly fluorinated polymers, which tend to be more soluble in pure NMP. This procedure afforded copolymers 4a-c with intrinsic viscosities ranging from 0.39 - 0.77 dL/g. Thus, the higher activity obtained with the DMPU solvent system provided a means by which copolymers derived from ortho-perfluoroalkylaryl fluorides could be obtained.
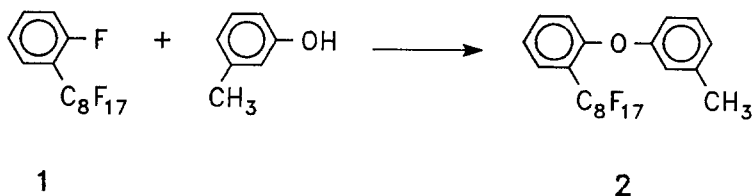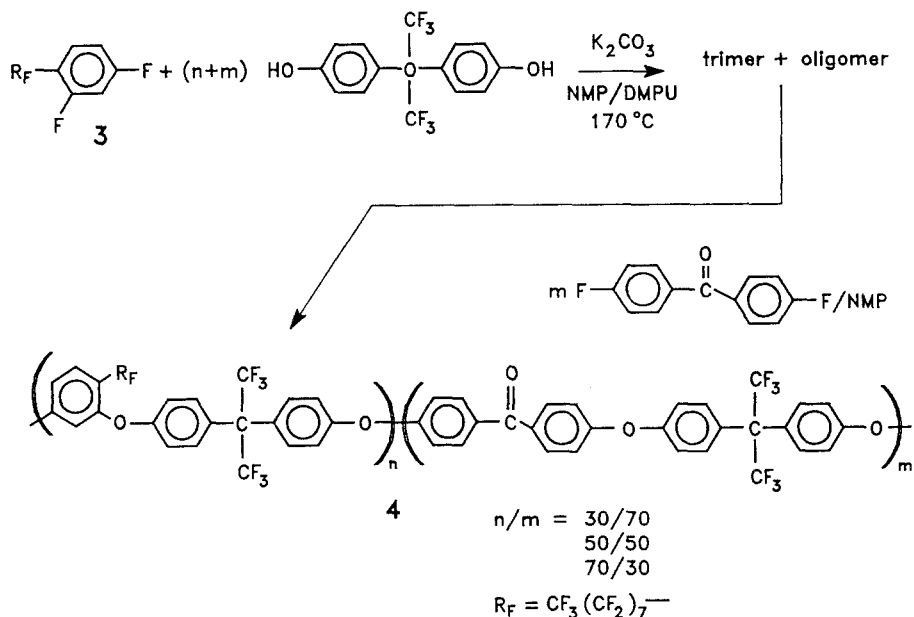
<div align="center"><b>Scheme I</b></div>



$$1 \qquad\qquad\qquad\qquad\qquad\qquad\qquad 2$$

Table 1

REACTION OF 1 WITH M-CRESOL[a]

| Solvent | T(°C) | %Yield of 2[b] | |
| | | 1 h | 24 h |
| --- | --- | --- | --- |
| NMP | 170 | 17 | 70 |
| DMPU | 170 | 15 | 90 |
| NMP:DMPU (2:1) | 170 | 26 | 84 |

a) $K_2CO_3$ base (b) GC yield, biphenyl internal standard

**Scheme II**



$$4 \quad n/m = 30/70$$
$$50/50$$
$$70/30$$
$$R_F = CF_3(CF_2)_7-$$

The advantages of DMPU as a reaction solvent also became evident in polymerizations involving heterocyclic-activated monomers which are less reactive than conventionally activated monomers. For example, 3,5-bis(4-fluorophenyl)-1,2,4-triazole (5) is less reactive than most activated fluorides, as indicated by H NMR chemical shift experiments (10). Model reactions of 5 with m-cresol at 170 °C showed full conversion in DMPU in 24 h,

**Scheme III**



| | Ar | [η] |
|---|---|---|
| **6a** : | –Ph(CH₃)₂Ph– | 0.43 |
| **b** : | –Ph(CF₃)₂Ph– | 0.55 |

| | |
|---|---|
| **7a** : | 3-NH₂ |
| **b** : | 4-NH₂ |
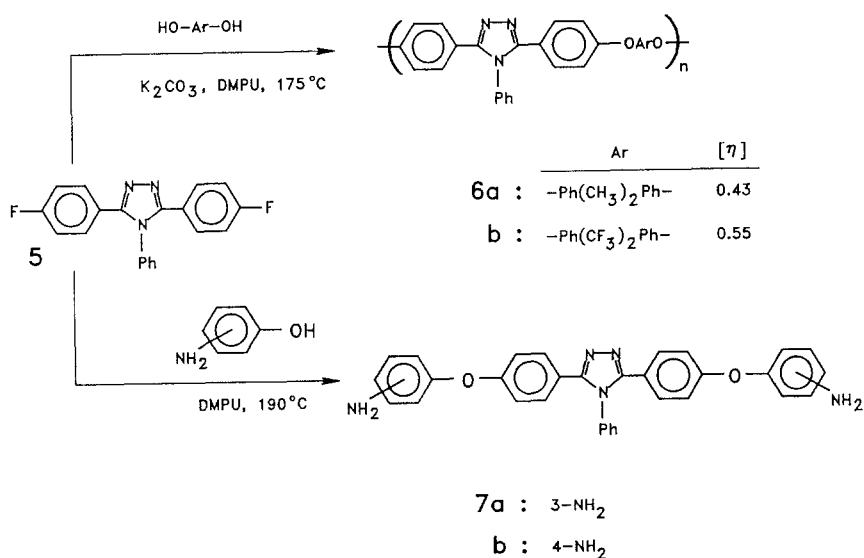
whereas a CHP/NMP solvent mixture required 72 h at 190 °C (10). The reaction using DMPU was observed not to discolor to the degree the reaction in NMP/CHP did, which became very dark. Polymerizations of **5** in DMPU at 175 °C were complete after 35 h, affording polymers **6a** and **6b** with intrinsic viscosities of 0.43 and 0.55 dL/g, respectively (Scheme III). In contrast, the polymerizations in NMP/CHP were maintained at 190 °C for 72 h, and afforded a polymer which could not be redissolved, presumably due to some crosslinking caused by the extended reaction time.

The synthesis of aromatic diamines derived from **5** and aminophenols were also more readily prepared in DMPU (11)(Scheme III). Reaction of **5** with 3- or 4-aminophenol took place in 16h in DMPU to afford the triazole derived diamines **7a** and **7b**, respectively. The analogous procedure in NMP/CHP required a 72 h reaction time for high conversion. Analogous to polymerizations using **5**, the reactions in DMPU afforded products which were noticeably lighter in color.

Another example of a heterocyclic-activated ether displacement facilitated by DMPU was the synthesis of polyethers using 2,3-bis(fluorophenylquinoxaline) (**8**) (12)(Scheme IV). This monomer differs from the earlier fluoroquinoxaline monomer (**9**) used in the synthesis of poly(aryl ether phenylquinoxalines) (15) in two ways: (1) the fluoro group is substituted on the pendent phenyl ring rather than the benzo ring of the quinoxaline nucleus, and (2) monomer **8** is obtained as one isomer rather than a mixture, as is the case with **9**. The result of these structural differences is that monomer **8**, is less reactive than **9**, consistent with the H NMR analysis, and the resulting polymer is less soluble in NMP than those derived from **9**, due to the lack of constitutional isomerism in the polymer backbone. Polymerizations were first carried out in NMP/CHP at 190 °C with bisphenol-A and bisphenol-AF. Polymerization times of 48 h were required to afford polymers **10a** and **10b**.

**Scheme IV**



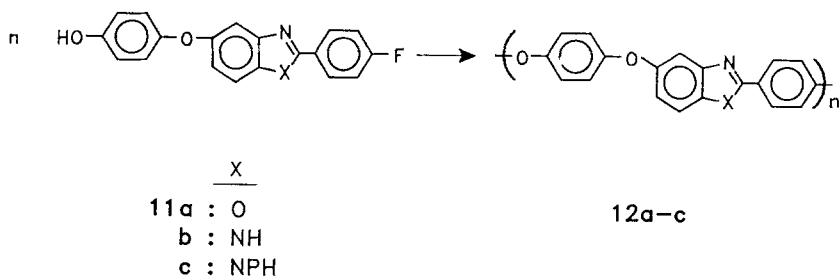| | Ar | $[\eta]$ |
|---|---|---|
| **10a** : | $-Ph(CH_3)_2Ph-$ | 0.55 |
| **b** : | $-Ph(CF_3)_2Ph-$ | 0.43 |



**9**
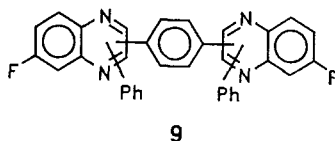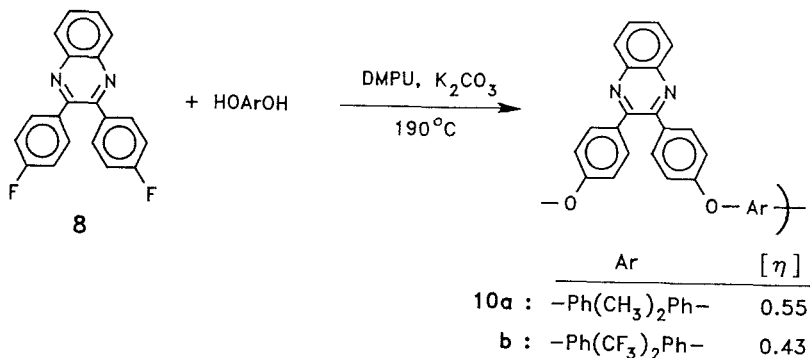
The polymers had intrinsic viscosities in the 0.3-0.4 dL/g range, and showed marginal solubility in the NMP/CHP solvent mixture, even though relatively flexible bisphenols were used. Conversely, when DMPU was substituted as the polymerization solvent a noticeable improvement in reaction rate and solubility were observed. Polymers **10a** and **10b** were obtained in 24 h with intrinsic viscosities of 0.55 and 0.43 dL/g, respectively.
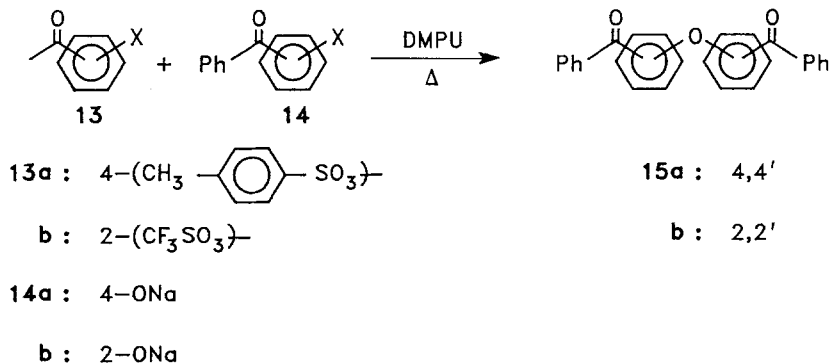
Self-polymerizations of several new A/B benzazole monomers were also investigated using DMPU as the solvent (13). Earlier work on poly(aryl ether benzazoles) had shown polymerizations involving more rigid bisphenols required high temperatures ($\simeq 250$ °C) to maintain solubility, and the resulting polymers were not readily soluble in NMP or CHP (16). This observation portended potential solubility difficulties in the self-polymerization of A/B benzazole monomer **11a** and benzimidizole monomers **11b** and **11c** (Scheme V), and led to the selection of DMPU as the solvent. Self-polymerization of **11a** was successfully carried out at 255 °C for 4 h, after dehydration with toluene, to afford high molecular weight poly(aryl ether benzoxazole) (**12a**) (intrinsic viscosity = 0.72 dL/g). Polymerization temperatures below 245 °C resulted in premature precipitation of the polymer. In the case of benzimidazole monomers **11b** and **11c**, polymerizations were carried out at 190 °C/20h and 180 °C/48h to afford poly(aryl ether benzimidazoles) **12b** and **12c**, respectively. The intrinsic viscosities measured were 0.60 dL/g and 0.45 dL/g for **12b** and **12c**, respectively.

A final example of the utility of DMPU as a reaction solvent for nucleophilic aromatic substitution was observed in the displacement of sulfonate leaving groups from activated aryl substrates (14). Although the triflate group was found to be a better leaving group than the fluoride, the tosylate was less reactive and required the use of DMPU to achieve quantitative yields. The reaction of 4-(benzoyl)phenyl tosylate (**13a**) with sodium 4-benzoylphenoxide (**14a**) required the use of DMPU to obtain complete conversion within 24 h (Scheme VI). Likewise, The reaction of 2-(benzoyl)phenyl triflate (**13b**) with sodium

**Scheme V**



| | X |
|---|---|
| **11a** : | O |
| **b** : | NH |
| **c** : | NPH |

**12a–c**

**Scheme VI**



| | | | | |
|---|---|---|---|---|
| **13a** : | 4–(CH$_3$ —⟨O⟩— SO$_3$)– | | **15a** : | 4,4' |
| **b** : | 2–(CF$_3$SO$_3$)– | | **b** : | 2,2' |
| **14a** : | 4–ONa | | | |
| **b** : | 2–ONa | | | |

2-benzoylphenoxide, which are less reactive owing to the ortho substitution, required the use of DMPU to achieve complete conversion to the ether **15b** (Scheme VI) It was also noted that the sulfone/ketone polyether copolymers prepared in this study tended to give hazy solutions in NMP, whereas DMPU solutions were clear.

The rationale for the higher reactivity observed for displacements in DMPU could be several-fold. Comparison of the dipole moments and dielectric constants of DMPU (17), DMAC and NMP (18) shows DMPU has the highest dipole moment as well as a high dielectric constant (Table 2). For nucleophilic substitution reactions, the reactivity of an anionic nucleophile is enhanced if the anion is exposed and not subject to ion-pairing. Ion pairing is generally low for solvents with a high dielectric constant (> 30). In addition, aprotic solvents with a large dipole moment are effective at coordination of cations affording more exposed highly reactive nucleophiles. The solvent parameters for the dipolar aprotic solvents in Table 4 suggest that the phenoxide anion will be more reactive in DMPU than in DMAC or NMP due to the high dipole moment and dielectric constant. This has been previously established in lithium-based carbanion chemistry, where Seebach showed DMPU is an effective HMPA substitute owing to its coordinative nature (7) Another possible factor may be that DMPU reduces the energy of activation required for formation of the Meisenheimer complex, which has been shown to be an important factor for the increased reaction rates in dipolar aprotic solvents vs protic solvents (4).

Table 2

SOLVENT PARAMETERS

| Solvent | Dielectric Constant | Dipole Moment(D) |
|---------|---------------------|------------------|
| NMP | 32.0 | 4.09 |
| DMAC | 37.8 | 2.72 |
| DMPU | 36.1 | 4.23 |

In summary, we have found DMPU to be an excellent solvent for nucleophilic aromatic substitution reactions and related polymerizations. The advantages are higher reaction rates and better polymer solubility, while presumably not presenting more of a health hazard than NMP. It's utility is particularly true in polymerizations involving less reactive substrates, and in systems where the resulting polymer shows marginal solubility in NMP or DMAC. Future work will include an evaluation of the five-membered ring analog of DMPU, N,N-dimethylethylene urea (DMEU), to determine if it affords similar enhancements in poly(aryl ether) synthesis.

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