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Synthesis of Poly(arylene ether)s Containing Triphenylamine Units via Nitro Displacement Reaction

Mong Sup Lee and Sang Youl Kim*

Center for Advanced Functional Polymers, Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology (KAIST), 373-1, Guseong-Dong, Yuseong-Gu, Daejeon 305-701, Korea

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Nucleophilic aromatic substitution (S_NAr) reaction has been known as one of the most efficient reactions for making aryl ether bonds and utilized in the synthesis of poly(arylene ether)s that have found application in many areas such as electronics and medical devices due to their good thermal stability, chemical resistances, and mechanical strength.[1] The S_NAr reaction generally requires a leaving group that is activated with an electron-withdrawing group at the para or ortho position.[2] Electron-withdrawing groups such as sulfone, ketone, heterocyclic rings, phosphine oxide, and perfluoroalkyl groups have been used in this reaction as an activating group, and poly(arylene ether sulfone)s, poly(arylene ether ketone)s, and poly(arylene ether imide)s are commercialized by the S_NAr reaction. Among the leaving groups, the nitro-leaving group shows a good leaving ability comparable to that of the fluorine-leaving group,[3] but the nitro displacement reaction should be performed at mild conditions because of the generation of nitrite ions that cause side reactions at elevated temperature.[4] Recently, we reported the synthesis of poly(biphenylene oxide)s via nitro displacement reaction at 190 °C.[5] Since the poly(biphenylene oxide)s consisting of the ether and aromatic linkages are stable to the attack of phenoxide nucleophiles, the nitro displacement reaction was feasible at high temperature.

The triphenylamine derivatives have been used as a hole transport layer in organic electroluminescence (OEL) devices[6] and second-order nonlinear optical (NLO) chromophores.[7] Since oligomeric and monomeric triphenylamines show low glass transition temperatures (T_g) which often induce thermal breakdown of the devices, it is desirable to develop the materials containing triphenylamines with high T_g and good thermal stability.[8] The incorporation of triphenylamine units into poly(arylene ether)s may produce a material with good thermal stability, high T_g, and a good processability, while maintaining the characteristics of triphenylamine units.

In this study, poly(arylene ether triphenylamine)s were synthesized from the monomer that has an electron-donating amine group at the para position of the nitro-leaving group. The S_NAr reaction requires a leaving group activated by a proper electron-withdrawing group, but the presence of any electron-donating group deactivates this reaction. The new monomer **1** has an electron-donating amine moiety at the para position of nitro-leaving group, even though the nitro-leaving group of the monomer is activated by the trifluoromethyl group at the ortho position. So, it is interesting to check the effect of the electron-donating amine moiety to the nitro displacement reaction in this case. The monomer **1** was synthesized through Pd-mediated amination of 5-bromo-2-nitirobenzotrifluoride with aniline, as shown in Scheme 1. Even though the combination of $Pd_2(dba)_3$ and BINAP in the presence of NaO^{t}Bu is known as a superior catalyst system for the cross-coupling of amines with aryl bromides,[9] K_3PO_4 was used as a base because the nitro groups cannot tolerate a strong base.

Scheme 1. Synthesis of Monomer

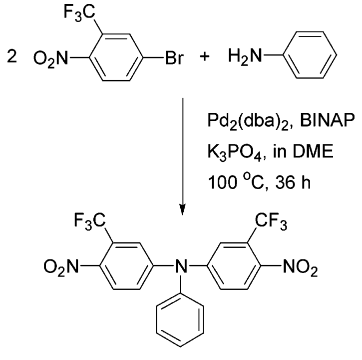

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Table 1. Properties of the Polymers

	$M_n^a/10^4$	$M_w^a/10^4$	PDI^a	T_g^b	T_{d5}^c
PAEA I	4.8	8.5	1.8	162	523
PAEA II	2.8	5.2	1.9	174	546
PAEA III	3.2	5.8	1.8	230	543

[a] Measured by GPC using THF as an eluent and polystyrenes as standards. [b] Measured by DSC with a heating rate of 10 °C/min in N_2. [c] 5% weight loss temperature measured by TGA with a heating rate of 10 °C/min in N_2.

To investigate the reactivity of the monomer, model reaction with *m*-cresol was studied. Interestingly, the model reaction began at 140 °C and completed at 180 °C within 2 h with quantitive yield. The chemical structure of the monomer and the model compound was confirmed by FTIR and NMR spectral analyses.[10] The side reactions caused by nitrite ions and phenoxides were not observed. The result of model reaction indicates that the chemical structure of monomer is stable to the attack of nucleophiles even at elevated temperature, presumably because the monomer does not have electron-deficient sites. It seems that the electron-withdrawing effect of the bulky trifluoromethyl group at the ortho position of the nitro-leaving group is strong enough to induce the formation of the Meisenheimer complex with the release of steric congestion, although the monomer has the electron-releasing amine group at the para position of the nitro-leaving group. Polymerizations of monomer **1** with bisphenol A, 4,4′-biphenol, and 4,4′-(9-fluorenylidene)diphenol were carried out successfully in anhydrous DMSO at 180 °C with K_2CO_3 (Scheme 2).

The chemical structure of poly(arylene ether triphenylamine)s was characterized by FTIR and NMR spectral analysis. After the polymerization, the peaks of NO_2 of the monomer at 1530 and 1341 cm^{-1} disappeared, but the peaks of C−O near 1235 cm^{-1} appeared in the FTIR spectra. All the carbons corresponding to

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* To whom correspondence should be addressed: Tel 82-42-869-2834; Fax 82-42-869-2810; e-mail kimsy@kaist.ac.kr.

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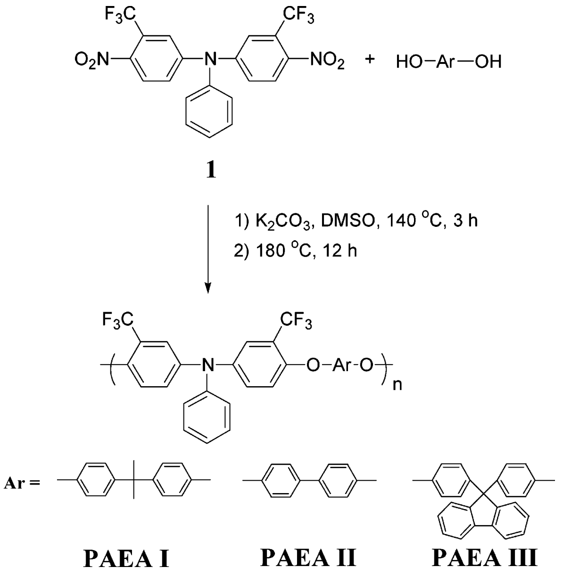
Table 2. Solubilities of the Polymers[a]

	NMP	DMAc	DMSO	EA	MC	THF	acetone	toluene	*m*-cresol
PAEA I	++	++	+	++	++	++	++	++	+
PAEA II	++	++	+	++	++	++	++	++	+
PAEA III	++	++	+	++	++	++	+−	++	+

[a] ++: soluble at room temperature; +: soluble at elevated temperature; +−: partially soluble.

Scheme 2. Polymerization



the polymer structure were observed in the ^{13}C NMR spectra. The number-average molecular weights of the polymers measured by GPC using THF as an eluent and polystyrenes as standards were in the range 28 000−48 000. Poly(arylene ether triphenylamine)s showed good thermal stability in TGA analysis. 5% weight loss of the polymers occurred above 523 °C. The T_g's of the polymers in DSC were observed at 162 °C (PAEA I), 174 °C (PAEA II), and 230 °C (PAEA III), depending on the bisphenols employed (Table 1).

The poly(arylene ether amine)s were dissolved well in common organic solvents including, THF, toluene, and acetone (Table 2).

It seems that the kinked structure of the triphenylamine moiety of the polymer main chains hinders the chain stacking of polymer induced by $\pi-\pi$ stacking, resulting in the amorphous polymers with improved solubilities. All the synthesized polymers formed a flexible and transparent film upon solution casting. The HOMO levels of the polymers measured by cyclic voltammetry were around −5.4 eV,[11] which are similar to that of *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) (~5.2 eV) measured in solution.[12]

In summary, poly(arylene ether triphenylamine)s were synthesized via nitro displacement reaction of the monomer, bis(4-nitro-3-trifluoromethylphenyl)phenylamine, with several bisphenols. Although the monomer has the electron-donating amine moiety at the para position of the nitro-leaving group, the high molecular weight polymers were obtained via the S_NAr reaction. The poly(arylene ether)s containing the triphenylamine moiety with high T_g and good thermal stability have a high application potential in organic electroluminescent devices.

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Supporting Information Available: Details of the experimental procedures, the spectral data for the monomer, FTIR, NMR, CV, and UV spectra, TGA and DSC thermograms of the synthesized polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The detailed synthetic procedure and the spectroscopic data of the monomer and the model compound are in the Supporting Information.

(11) The band gaps of polymers, calculated from absorption band edges of 393, 392, and 392 nm in UV−vis spectra, are 3.15, 3.16, and 3.16 eV, respectively. The HOMO levels of polymers were calculated from cyclic voltammetry using the ferrocene value of −4.8 eV as a standard.

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