Macromol. Symp. **2004**, *216*, 109-115

Synthesis and Characterization of a Novel Poly(aryl ether) Containing 4-Chloro-2,5-diphenyloxazole

Nuttaporn Pimpha,[1] *Supawan Tantayanon,**[1] *Frank Harris*[2]

[1] Functional Polymer and Petrochemistry Laboratory, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
E-mail: supawan.t@chula.ac.th
[2] The Maurice Morton Institute of Polymer Science, Akron University, Ohio, USA

Summary: 4-Chloro-2,5-bis(4-fluorophenyl)oxazole monomer has successfully been synthesized using cyclization reaction of 4-fluorobenzoyl cyanide with 4-fluorobenzaldehyde. This monomer was converted to poly(aryl ether)s by nucleophilic substitution of the fluorine atoms on the benzene rings of oxazole monomer with bisphenol A. The influence of the reaction time on the molecular weight had been investigated. The polymers were identified by FT-IR, ^{1}H-NMR and TGA. The products exhibited weight-average molar masses up to 2.81 x 10^4g mol^{-1} in GPC. These poly(aryl ether)s showed very high thermal stability up to 363 °C for 5 % weight loss in TGA under N_2.

Keywords: 2,5-diphenyloxazole; poly(aryl ether); poly(aryl ether oxazole)

Introduction

Poly(aryl ether)s are well-known high-performance engineering thermoplastics. These materials have interesting physical properties, including a high modulus, toughness, high thermal and thermooxidative stability, and chemical resistance.[1] It has been shown that aromatic nucleophilic substitution reaction between activated aryl halide monomer and bisphenoxides can lead to the formation of linear poly(aryl ether)s.[2-3] Thus, the halogens must be activated, which is achieved by the presence of an electron withdrawing group in the para position. Heterocyclic rings can serve as activating groups to decrease the electron density in the para position of adjacent phenyl rings.[4-13]A common feature of these groups is stabilization negative charges developed at the 2- or 4-position of aryl moiety in the transition state of the nucleophilic halogen displacement reaction. Among the heterocyclic rings, 2,5-diphenyloxazole is particularly interesting because it is highly fluorescent and, thus, has potential in fluorescent sensors, laser dyes and scintillators for detecting nuclear radiations.[14-20] Because of these interesting properties of 2,5-diphenyloxazole, considerable

DOI: 10.1002/masy.200451212

attention has been devoted to the preparation of a new classes of 2,5-diphenyloxazole containing polymers.

The 2,5-bis(4-fluorophenyl)oxazole monomer is extremely reactive, because the fluorine atom is activated not only by the negative inductive effect but also by the electron deficiency of the oxazole ring and therefore produces high molar mass poly(aryl ether)s when reacted with bisphenol A.[21] Numerous methods for the preparation of oxazole rings with various substitution patterns have been reported. For example, the cycloaddition reaction of benzonitriles and benzoyl chloride led to the formation of the polymer. However, such synthesis involve several steps and the difficultly to handle CH_2N_2. In this research, the much simple method has been used to synthesize 4-chloro-2,5-bis(4-fluorophenyl)oxazole. We chose to synthesize our monomers according to a modification of Fischer synthesis[22] from the 4-fluorobenzoyl chloride and 4-fluorobenzaldehyde in one step. The objective of this work was the synthesis of poly(aryl ether) containing 4-chloro-2,5-bis(4-fluorophenyl)oxazole was to be prepare and polymerized with bisphenol A.

Experimental

Materials

4-Fluorobenzaldehyde, 1,3-dimethyl-3,4,5-tetrahydro-2(1H)-pyrimidinone (DMPU) and 4-fluorobenzoyl chloride (Aldrich Chemical Co.) were used as received. Potassium carbonate and cuprous cyanide (Fischer Chemical Co.) were ground and dried at 100°C under reduced pressure overnight before use. Bisphenol A (Aldrich Chemical Co.) was recrystallized from methanol. Toluene (Fischer Chemical Co.) was dried with magnesium sulfate overnight before use. Tetrahydrofuran was freshly distilled from sodium/benzophenone.

Instrumentation

Thermogravimetric analyses (TGA) were carried out under nitrogen at a heating rate of 10°C/min using a TA instrument model 2950 thermogravimetric analyzer. Gel permeation chromatography (GPC) was carried out on a Jasco 880-PU system with Jasco UV-970 Detector. Calibration was done with standard polystyrene samples. Tetrahydrofuran was used as the eluant at a flow rate of 1 mL min^{-1} at 28°C. ^1H NMR and ^{13}C NMR spectra were recorded on a Brucker AC200 spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) were reported in parts per million relative to the residual signals of this solvent (δ 7.24 for ^{1}H and δ 77.0 for ^{13}C). Infrared spectra were recorded on an Impact 410 Nicolet FT-IR spectrometer as a solid suspended in a potassium bromide disk. Melting points were measured using an Electrothermal 9100 melting point apparatus.

Synthesis of 4-Chloro-2,5-bis(4-fluorophenyl)oxazole

4-Fluorobenzoyl cyanide (25 mmol, 3.72g) and 4-fluorobenzaldehyde (20 mmol, 3.10 g) in 50 mL dry THF were contained in a reaction flask which was connected to a HCl gas generator. The reaction mixture was allowed to cool in an ice-NaCl cooling bath to 0°C and then dry HCl gas was passed into the solution until the HCl gas was no longer absorbed by the reaction mixture(3 hours), tested by ammonia at the outlet of the reaction flask. At this stage, the reaction flask was quickly sealed and kept at 0°C for 2 days. The reaction mixture was then poured onto an ice with continuous stirring and subsequently filtered. The product was recrystallized from 1:1 mixture of hexane/ethylacetate to afford white crystals.(2.36 g, 44%) mp 110°C. MS m/z: 292. IR (KBr): ν (cm^{-1}): 3035, 1621, 1530, 1494, 1439, 1399, 1337, 1238, 1120, 1056, 905, 850, 644 and 524. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.09 (4H, m) and 7.13 (4H, m). ^{13}C NMR (200 MHz, $CDCl_3$): δ (ppm) 164.4, 163.1, 160.8, 150.9, 138.5, 132.1, 128.7, 126.4, 124.8, 124.3 and 116.4.

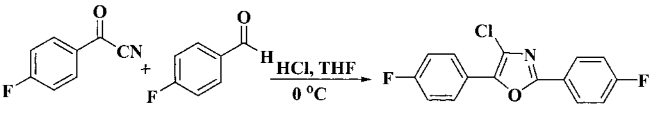
Polymerization

Oxazole monomer (0.73 g, 2.5 mmol) and bisphenol A (0.57 g, 2.5 mmol) were dissolved in 20 mL of DMPU and 10 mL of toluene under nitrogen in a round-bottom flask with a reflux condenser, a nitrogen inlet, and a Dean-Stark trap. Potassium carbonate was added (0.75 g, 5.1 mmol), and the mixture was refluxed for 3 h at 180 °C in an oil bath temperature. During refluxing, fresh and dry toluene was refilled twice. Finally, the temperature was raised to 220 °C while the toluene was removed through the Dean-Stark trap. After 12 h, 1 mL of acetic acid was added to neutralize the phenoxide, and the mixture was filtered hot to remove salts. After the reaction was cooled to ambient temperature the polymer was precipitated by pouring the mixture into a mixture of 450 mL of methanol and 50 mL of water. The polymer was filtered off, washed with water and methanol and dried under reduced pressure. IR (KBr): ν (cm^{-1}): 3052, 1608, 1512, 1486, 1473, 1333, 1250, 1207, 1174, 1132, 1053 and 824. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05(m), 7.65(m), 7.25(m), 7.05(m), 6.95(m) and 1.71(s).

Results and Discussion

Synthesis of monomer

To synthesize 4-chloro-2,5-bis(4-fluorophenyl)oxazole, 4-fluorobenzoyl cyanide has firstly been obtained from nucleophilic substitution reaction between 4-fluorobenzoyl chloride and cuprous cyanide.[23] It was then reacted with 4-fluorobenzaldehyde as shown in Scheme 1.

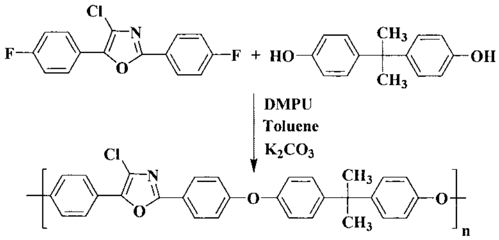


Scheme 1. Reaction scheme and structure of 4-chloro-2,5-bis(4-fluorophenyl)oxazole monomer.

The IR spectrum of this product confirmed the existence of an oxazole ring as shown by a strong absorption band at 1530 cm^{-1} assigned to the –N=C-O- ring stretching frequency. The mass spectrum of this compound contained m/z peaks corresponding to the calculated molecular weights of 292 and 294 with the ratio of 3: 1 due to the presence of chlorine in the molecule. ^{1}H and ^{13}C NMR data also indicated the structure of 4-chloro-2,5-bis(4-fluorophenyl)oxazole. In particular, it was clearly revealed by the ^{13}C signals at 160.8 (C2), 150.9 (C4) and 138.5 (C5) ppm which are the characteristic ^{13}C pattern for 4-chloro-2,5-diphenyloxazole compounds synthesized in our laboratory. The ring formation has been proposed to occur via the formation of acylimidoyl chloride and then reacted further with the carbonyl carbon of the aldehyde. Apparently, 4-chloro-2,5-bis(4-fluorophenyl)oxazole can successfully be synthesized in one step with a simple work-up. It should be noted that the fluorine of 4-fluorobenzaldehyde served as the electron donating group in this reaction which retarded the ring formation. That's the reason why, the reaction afforded only 44% yield. This explanation can be supported by another reactions between benzoyl cyanide and several other 4-substituted benzaldehydes. For examples, the reaction of benzoyl cyanide with 4-dimethylaminobenzaldehyde and terephthalaldehyde gave 20% and 70% yield, respectively. The synthesis of the 4-chloro-2,5-diphenyloxazole compounds and the mechanism of their formation will be reported in a separate paper.[24]

Synthesis of polymer

Polymerization of the 4-chloro-2,5-bis(4-fluorophenyl)oxazole with stoichiometric amounts of bisphenol A was carried out in the presence of potassium carbonate in DMPU/toluene as shown in Scheme 2.



Scheme 2. Reaction scheme of the poly(aryl ether) containing 4-chloro-2,5-bis(4-fluorophenyl)oxazole unit.

During the initial stage of the polymerization, the reaction temperature was maintained at 180-200°C to convert bisphenol A to its salt. The reaction was drived by the removal of water from yhe reaction mixture as the azeotropic mixture with toluene via a Dean-Strak trap. Upon completion of the salt formation and dehydration, the reaction temperature was raised to 220°C to effect the nucleophilic displacement. The influence of polymerization time on molecular weight of the polymer was observed. At lower reaction time, the lower molecular weightof the polymer was obtained as shown in Table 1.

Table 1. Polymerization results at different reaction time.

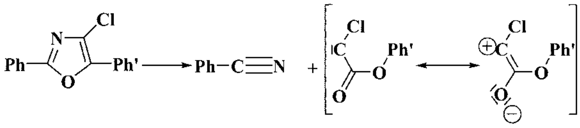
Reaction time (h.)	Mw (g/mol)	TGA (5% weight loss)
3	17,844	341
6	13,295	334
9	28,118	363
12	13,115	359

This was presumably due to the lack of sufficient time necessary to maximize the chain growth. At polymerization time greater than 9 h, however, the decrease in molecular weight was resulted. It was probably caused by three possible chain scissions, the attack of KF and the carbonate from base at the polymer chains and transetherification. Similar results on condensation polymerization of the other aromatic difluoride with phenoxides has been reported.[25]

Thermal stability

The poly(aryl ether)s exhibit excellent thermal stability as summarized in Table 1. These polymers showed a 5% weight loss at the temperature ranging from 334 to 363°C as determined by dynamic TGA. Maier et al. reported that similar poly(aryl ether oxazole) without a chlorine group on an oxazole unit exhibited decomposition temperatures at 466 °C in nitrogen atmosphere.[8] The source of the instability of the oxazole ring in the polymers can be found by studying the synthetic routes to oxazoles.

Cycloaddition reactions are known to be reversible at high temperatures and therefore oxazoles may be subject to this kind of decomposition reaction to benzonitrile and ketonecarbene. In the case of P_1 and P_2, one of the two most important mesomeric structures of the ketocarbene is strongly stabilized by chlorine. Therefore, the activation energy for the cycloreversion of the chlorinated oxazole is lower than that for the cycloreversion of the unsubstituted oxazole, and hence the decomposition of the chlorinated oxazole starts at lower temperatures.



ketonecarbene

Solubility

All poly(aryl ether)s containing 4-chloro-2,5-diphenyloxazole show good solubility in a number of common organic solvents. Table 2 summarizes the results of qualitative solubility tests which were attempted to obtain 10% w/v solutions of the polymers in various solvents. They were easily soluble in a number of common organic solvents including THF and chloroform, as well as in more polar amidic solvent such as NMP.

Table 2. Solubility tests with the Poly(aryl ether oxazole)s.

Reaction time	NMP	DMSO	THF	Acetone	$CHCl_3$	Toluene
3	+	+	+	+	o	o
6	+	+	+	+	o	o
9	+	+	+	+	o	o
12	+	+	+	+	o	o

(+) soluble at room temperature
(o) soluble on heating

Conclusion

In this paper, we reported here a new 4-chloro-2,5-bis(4-fluorophenyl)oxazole monomer which has been synthesized using cyclization reaction between 4-fluorobenzoyl chloride and 4-fluorobenzaldehyde. Polymer synthesis was successful and the 4-chloro-1,3-oxazole can activate nucleophilic displacement in the synthesis of poly(aryl ether oxazole)s. The optimum polymerization time to obtain a high molecular weight up to 2.63×10^5g mol^{-1} was 9 hour. A 5 % weight loss occurred between 334-363°C in TGA under N_2.

Acknowledgments

The authors of this paper would like to thank the Thailand Research Fund under the Golden Jubilee number PHD/225/2541 for financial support of this research.

[1] Susanta, B.; Maier, G. *Chem Mater.***1999**, 11, 2179.
[2] Susanta, B.; Maier, G.; Martin, B. *Macromolecules.* **1999**, 32, 4279.
[3] Maiti, S.; Mandal, B. *Prog. Polym. Sci.* **1986**, 12,111.
[4] Hedrick, J.L.; Twieg, R. *Macromolecules.* **1992**, 25, 2021.
[5] Hedrick, J.L.; Labadie, J.W. *Macromolecules.* **1988**, 21, 1883.
[6] Arnold, F.E.; Van Deusen, R.L. *Macromolecules.* **1969**, 2, 497.
[7] Blaise, C.; Bouanane, A.; Brembilla, A.; Lochon, P.; Neel, J. *J. Polym. Sci., Polym. Symp.* **1975**, 52, 137.
[8] Maier, G.; Schneider, J. M. *Macromolecules* **1998**, 31, 1798.
[9] Hedrick, J. L. *Macromolecules.***1991**, 24, 6361.
[10] Saegusa, Y.; Iwasaki, T.; Nakamura, S. *J.Polym. Sci., Part A: Polym. Chem.* **1994**, 32, 249.
[11] Hedrick, J. L.; Labadie, J. W. *Macromolecules.***1990**, 23, 2223.
[12] Hedrick, J. L.; Jonsson, H.; Karter, K. R. *Macromolecules.* **1995**, 28, 4342.
[13] Hilborn, J. G.; Labadie, J. W.; Hedrick, J. L. *Macromolecules.* **1990**, 23, 2854.
[14] Clapman, B.; Sutherland, A. J. *Tetrahedron Lett.* **2000**, 41, 2257.
[15] Clapman, B.; Sutherland, A. J. *Tetrahedron Lett.* **2000**, 41, 2253.
[16] Hiromitsu,I.; Tomiki,I.; Kunihiro,I. *Macromolecules.* **1993**, 26, 4533.
[17] Clapman, B.; Richards, A. J.; Wood, M. L.; Sutherland, A. J. *Tetrahedron Lett.* **1997**, 38, 9061.
[18] Horrocks, D. L. *Applications of Liquid Scintillation Counting*, Academic Press, New York, **1974**, 51.
[19] McCairn, M. C.; Hine, A. V.; Sutherland, A. J. *J. Mater. Chem.* **2003**, 13, 225.
[20] Hamerton, I.; Hay, J. N.; Jones, J. R.; Lu, S. *J. Mater. Chem.* **1998**, 8, 2429.
[21] Maier, G.; Hecht, R.; Nuyken, O.; Helmereich, B.; Burger, K. *Macromolecules* **1993**, 26, 2583.
[22] Micheal, D.; Ram,L.; Bela,T. *J.Heterocyclic Chem.*, **1977**, 14,317.
[23] Oalewood, T. S.; Weizgerber, C. A. *Organic Syntheses.* Coll 3, 113.
[24] Pimpha, N.; Tantayanon, S. *Heterocycles.* Accepted for Publication.
[25] Klein, D. J.; Modarelli, D. A.; Harris, F.W. *Macromolecules* **2001**, 34, 2427.