Preparation of Polyenaryloxynitriles from Dicyanovinyl Chloride and Diphenol Derivatives in the Presence of DABCO

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The kinetic study of the enaryloxynitriles *via* the nucleophilic vinylic substitution reaction of various phenol derivatives with 1-chloro-1-phenyl-2,2-dicyanoethene (1) was conducted in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO). Nucleophilic vinylic substitution of phenol derivatives with electrophilic olefins carrying sluggish leaving group involves a third-order reaction. The reaction was applied to solution polymerization of diphenol derivatives with p-bis(1-chrolo-2,2-dicyanovinyl)benzene (2), which yielded various polyenaryloxynitriles with moderate molecular weight.

Introduction

An early attempt to characterize the behavior of atoms in an atom assembly by a parameter was the concept of electronegativity formulated by L. Pauling.[1] One of the most powerful electronegativity-enhancing groups is the cyano group. The more C≡N groups a carbon atom bears, the greater will be its attraction for electrons. Dicyanomethylidene (=C(CN)$_2$) group and the carbonyl oxygen atom have similar inductive and resonance effects. The dicyanomethylidene group can be considered structurally equivalent to the carbonyl group in reactions where the two functional groups have similar inductive and resonance effects.[2,3] Many well-known reactions with carbonyl groups including Fries shift, Friedel-Crafts synthesis and Curtius-analogous rearrangement have been shown to have close parallels with the dicyanomethylidene group.[3] Thus, enaryloxynitriles can be considered analogous to ester.

Nucleophilic vinylic substitution reaction of 2,2-dicyanovinyl chloride occurred by various mechanistic pathways. In the most investigated addition-elimination route, the primary nucleophilic attack on the double bond is followed by an expulsion of the leaving group.[4-11] 2.2-Dicyanovinyl chloride reacts with amine, in most cases by a two step addition-elimination mechanism, to produce enaminonitrile.[12] Phenoxide have been considered as nucleophiles for the enaryloxynitriles, which has been applied to the interfacial polymerization of diphenol derivatives with p-bis(1-chrolo-2,2-dicyanovinyl)benzene to give polyenaryloxynitriles.[13-19] But phenol itself can react with dicyanovinyl chloride in the presence of tertiary amine as if the acid chloride reacted with phenol derivatives.

DABCO catalyzed nucleophilic vinylic substitution reaction of 1 with various phenols has been recently carried out to form enaryloxynitriles derivatives.[20] This synthetic method can be applied to the preparation of polyenaryloxynitriles by solution polymerization technique.

This article deals with the preparation of polyenaryloxynitriles *via* the nucleophilic vinylic substitution reaction of diphenols with 2 along with the kinetic study of the reaction of 1 with phenol derivatives in the presence of DABCO.

Experimental Section

Materials and Instruments. 1-Chloro-2,2-didicyanoethene (1) and 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (2) were prepared by the literature method reported previously.[12] Phenol. p-methoxyphenol, p-hydroxybenzaidehyde, p-nitrophenol, 1,4-diazabicyclo[2.2.2]octane. bisphenol A. (Aldrich Chem. Co.) were used without further purification. 1,5-Bis (p-hdroxyphenoxy)pentane was prepared by the method previously reported.[21] N-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation after drying by azeotropic distillation with benzene using Dean-Stark separator.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer. Fourier-transform infrared (FT-IR) spectra were taken on a Midac model M-1200 spectrometer. The gas chromatogram were obtained with a Varian star 3400 gas chromatography (GC). Elemental analysis data were obtained with Yanaco-MT-3 CHN analyzer.

Representative Preparation of 1-Phenoxy-1-phenyl-2,2-dicyanoethene (3). In a three-necked round-bottomed flask equipped with a dropping funnel. a condenser and a nitrogen inlet system, was placed a solution of phenol (0.25 g, 2.65 mmol) and DABCO (0.30 g, 2.65 mmol) in dry NMP (10 mL). After the solution was purged with nitrogen. a solution of 1 (0.5 g, 2.65 mmol) in NMP (10 mL) was added dropwise at 20 °C for 5 min. The stirred mixture was heated to 60 °C and maintained for 24 h. After the reaction mixture was subsequently poured into water. the powdery product was filtered and was recrystallized from isopropyl alcohol. The similar procedures were applied to synthesize other enaryloxynitriles 4-6.

3: Yield 85%. mp 139.5-140 °C. IR (KBr): 3022 (C-H), 2219 (C≡N). 1585 (C=C). 1250-1100 (C-O) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.4-7.7 (m 5H, *Ph*-). 7.0-7.2 (m. 5H -O-*Ph*). ^{13}C NMR (CDCl$_3$) δ 71.2 (=C(CN)$_2$), 111.3, 113.1 (-CN). 122.5, 128.0, 129.6, 130.1, 132.8, 151.5 (aromatic *C*'s). 180.7 (=*C*-O-).

4: Yield 95%. mp 148 °C. IR (KBr): 3027 (aromatic C-H), 2980 (aliphatic C-H). 2225 (C≡N). 1565 (C=C). 1224-1120 (C-O) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.5-7.7 (m, 5H, *Ph*-). 6.9-7.2 (m, 4H, -O-*Ph*-OCH$_3$). 3.7 (s, 3H, C*H$_3$*-O-Ph-).

5: Yield 75%. mp 130 °C. IR (KBr): 3022 (C-H), 2221

(C≡N), 1580 (C=C), 1782 (C=O), 1280-1120 (C-O) cm⁻¹. ¹H NMR (CDCl₃) δ 9.9 (s, 1H, Ph-C*H*O), 7.3-7.5 (m, 5H, *Ph*-), 7.7-7.9 (m, 4H, -*Ph*-CHO).

6: Yield 68%. IR (KBr): 3022 (C-H), 2221 (C≡N), 1580 (C=C), 1552 (N=O), 1250-1120 (N-O, C-O and C-N) cm⁻¹. ¹H NMR (CDCl₃) δ 7.5-7.8 (m, 5H, *Ph*-), 8.1-8.4 (m, 4H, -*Ph*-NO₂).

Kinetics. The reactions proceeded by monitoring the appearance of the enaryloxynitriles using a Varian Star 3400 gas chromatography (GC). All reactions performed under third-order conditions in which the DABCO concentrations were in the same concentration of the substrate. The reaction solutions were prepared by dissolving 1-chloro-1-phenyl-2,2-dicyanoethene and phenol, which was also the same quantity of the substrate. The reaction medium was NMP containing DABCO as a acid acceptor. All the solutions were prepared freshly just before use under nitrogen atmosphere and transferred by micro-syringe.

Polymerization and Copolymerization. In a three-necked round-bottomed flask equipped with a dropping funnel, a condenser and a nitrogen inlet system, was placed a solution of bisphenol A (1.50 g, 6.6 mmol) and DABCO (0.74 g, 6.6 mmol) in dry NMP (10 mL). After the solution was purged with nitrogen, a solution of **2** (2.0 g, 6.6 mmol) in NMP (10 mL) was added dropwise at 20 °C for 5 min. The stirred mixture was heated to 60 °C and maintained for 24 hr. After the reaction mixture was subsequently poured into water, the powdery polymer was collected by filtration and washed with methanol/water (1/1). The THF solution was reprecipitated into hexane to produce a yellow powdery polymer. The similar procedures were applied to synthesize other poly-enaryloxynitriles **8** and **9**.

7: Yield 86%. IR (KBr): 3050 (C-H), 2220 (C≡N), 1580 (C=C), 1330, 1250-1110 (C-O) cm⁻¹. ¹H NMR (DMSO-d_6) δ 7.5 (s, 4H, *aromatic H's*), 6.8-7.2 (m, 8H, *aromatic H's* in bisphenol A), 1.4 (s, 6H, 2 -C*H₃*). ¹³C NMR (DMSO-d_6 + CDCl₃) δ 30.6, 42.6, 72.5, 110.3, 112.2, 114.9, 119.3, 127.6, 128.6, 130.6, 148.8, 151.7, 178.0. Anal. Calcd for C₂₉H₁₈N₄O₂: C, 76.65; H, 3.96; N, 12.33. Found: C, 76.98; H, 4.01; N, 12.29.

8: Yield 92%. IR (KBr): 3122, 2915 (C-H), 2220 (C≡N), 1578 (C=C), 1300, 1245-1110 (C-O) cm⁻¹. ¹H NMR (DMSO-d_6 + CDCl₃) δ 7.5 (br, 4H, *aromatic H's* in **2**), 6.8-7.2 (m, 8H, *aromatic H's* in diphenol), 3.8 (br, 4H, -O-C*H₂*CH₂CH₂-CH₂CH₂O-), 1.2-1.8 (m, 6H, -O-CH₂C*H₂*C*H₂*CH₂CH₂O-). Anal. Calcd for C₃₁H₂₂N₄O₄: C, 72.37; H, 4.28; N, 10.89. Found: C, 72.35; H, 4.29; N, 10.79.

9: Yield 89%. IR (KBr): 3050 (C-H), 2220 (C≡N), 1580 (C=C), 1330, 1250-1110 (C-O) cm⁻¹. ¹H NMR (DMSO-d_6 + CDCl₃) δ 7.5 (br, 4H, *aromatic H's* in **2**), 6.8-7.2 (m, 8H, 1/2 *aromatic H's* in bisphenol A and 1/2 *aromatic H's* in diphenol), 3.8 (br, 2H, 1/2 -O-C*H₂*CH₂CH₂CH₂CH₂O-), 1.4 (s, 3H, 1/2 2 -CH₃). Anal. Calcd for C₃₀H₂₀N₄O₃: C, 74.38; H, 4.13; N, 11.57. Found: C, 74.28; H, 4.14; N, 11.54.

Results and Discussion

We have already reported that the enaryloxynitriles and

R: H,   OCH₃,   CHO,   NO₂
3   **4**   **5**   **6**
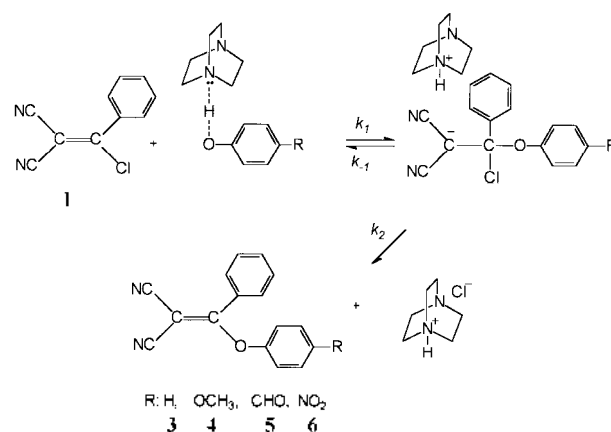
Scheme 1

polyenaryloxynitriles were obtained by two phases solvent system using phase transfer catalyst.[13] In this study, various enaryloxynitriles were prepared by the reaction of **1** with phenol derivatives in the presence of DABCO. After 24 h, good yields of enaryloxynitriles were obtained. The results and conditions of preparation of various enaryloxynitriles are summarized in Table 1.

In the ¹H NMR spectra, the phenyl protons in **1** appeared as a multiplet peak centered at 7.5 ppm, whereas those of phenol were present as a multiplet at 7.2 ppm. The enaryloxynitriles derived from phenol derivatives such as *p*-methoxyphenol showed singlet peak at 3.7 ppm corresponding to methoxy group. The reactivity of various phenols to **1** was variable according to the pK_a values of the corresponding phenol. In the case of *p*-methoxyphenol, the reaction proceeded rapidly to give 1-(4-methoxyphenoxy)-1-phenyl-2,2-dicyanoethene in good yield. Phenoxide derived from *p*-methoxyphenol was highly effective for the nucleophilic vinylic substitution reaction, because of the improvement of electron donation by the substituent at para-position. On the other hand, *p*-hydroxybenzaldehyde and *p*-nitrophenol proceeded at a slower rate because of its high pK_a value 7.62 and 7.17, respectively. The results of reaction of **1** with various phenol derivatives were summarized in Table 1.

The rate of DABCO catalyzed reaction between **1** and phenol derivatives was measured in NMP at 60 °C by gas chromatography. It was found that the reaction of phenol with electrophilic olefins carrying sluggish leaving group involves a third-order term. The initially formed anion is followed by expulsion of chloride anion via back donation. The third-order rate coefficient for the product -d[**1**]/dt = k_{obs}[**1**]

Table 1. Results of reaction of **1** with various phenol derivatives

Phenols	Substituent[a]	pK_a	Yield (%)[b]
3	H	9.99	85
4	MeO	10.20	95
5	CHO	7.62	75
6	NO₂	7.17	68

[a]para-position of phenol derivative. [b]Yields were determined gravimetrically after recrystallization.

[phenol][DABCO] is given by Eq. (1) according to the Scheme 1. The reaction was found to obey the following rate expression.

$$k_{obs} = \frac{k_1[1][phenol][DABCO]}{(k_{-1} + k_2)[1 + \text{Phenoxide anion}][\text{DABCO salt}]} \quad (1)$$

When $k_2 \gg k_{-1}$, k_{obs} is given by equation $k_{obs} = k_1$. This result indicated that there is significant contribution of DABCO from the mechanism, which involves an expulsion of chloride anion. We now extend our work to other phenol reactants with different acidity by changing the substituents of phenol. Comparison of our data with measurements on the same reaction using substituted phenolic compounds, electron-donating group at para-position increased the reactivity of the phenol derivative to dicyanovinyl chloride. This effect may be caused by the increase in the partial negative charge on the oxygen atom bearing the benzene ring, rendering this position more nucleophilic. The experimental conditions and third-order rate constant for the reaction of **1** with phenol derivatives were summarized in Table 2 and Figure 1.

The displacement of the vinylic halogen by four phenols was followed by gas chromatographically in NMP solvent

by observing the integration of the product enaryloxynitriles. The reactions were overall of the third-order (with rate coefficient k_{obs}), first order each in the vinyl halide, phenol and DABCO, with no apparent trend of the increase in k_{obs} with the increase in the amine concentration.

Brønsted plots of logk_{obs} against the pK_a of the para-substituted phenols are shown in Figure 2. The slope is somewhat deviated from the linearity. The value of logk_{obs}/pK_a is within 0.198-0.422.

Bisphenol A and 1,5-bis(p-hydroxyphenoxy)pentane were adopted as starting materials. The Scheme 2 outlines the solution polymerization of **2** with aromatic diols in the presence of DABCO in NMP solution.

Diphenol derivatives in this experiment showed a sufficient nucleophilicity to dicyanovinyl chloride. Bisphenol A and 1,5-bis(p-hydroxyphenoxy)pentane have pK_a value 10.26 and 10.20, respectively.

The results of polymerization of **2** with diphenols are sum-

Table 2. Experimental conditions and third order rate constant for the reaction of **1** with phenol derivatives in the presence of DABCO in NMP

X	[1]/10^{-3}	[X-PhOH]/10^{-3}	[DABCO]/10^{-3}	$k_{obs}/10^{-6}$
H	5.01	5.00-24.53	5.00-24.53	1.21-5.10
p-MeO	4.21	4.20-20.21	4.20-20.21	2.91-15.13
CHO	5.48	5.50-27.32	5.50-27.32	0.41-2.05
NO₂	5.54	5.61-27.50	5.61-27.50	0.15-0.75
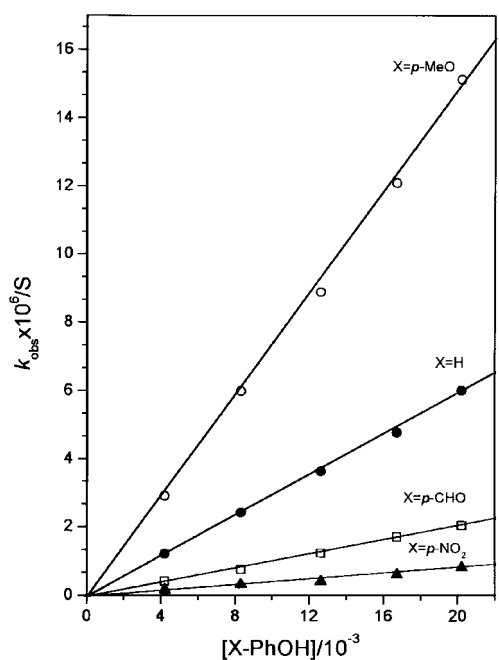
Figure 1. Plots showing dependence of k_{obs} on the concentration of nucleophiles for the reaction of 1-chloro-phenyl-2,2-dicyanoethene with phenol derivatives in the presence of DABCO in NMP.
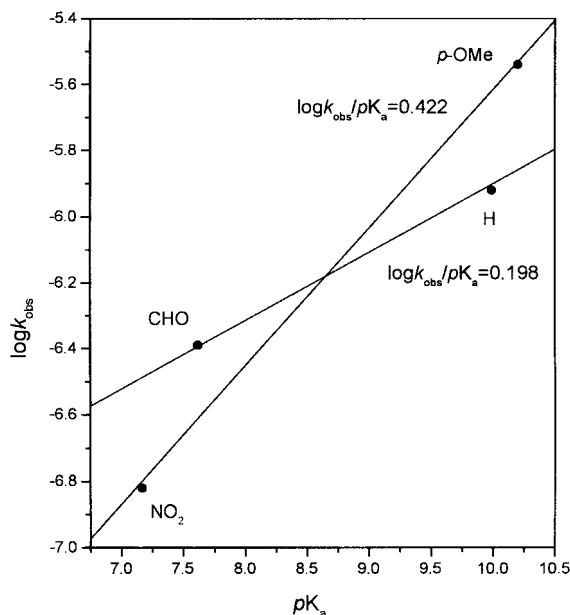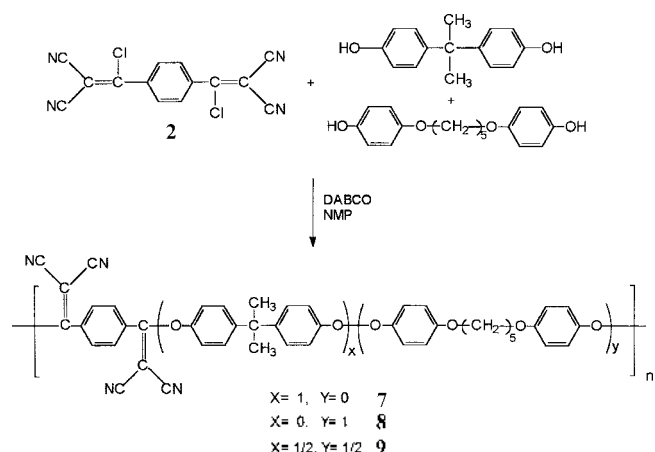

Figure 2. Brønsted-type plots for the reaction of **1** and diphenol derivatives in the presence of DABCO in NMP at 60 °C.

Scheme 2

Table 3. Results of polymerization of **2** with diphenols in the presence of DABCO

Polymers	pK_a	MW^a	MWD	η_{inh}^b	Yield (%)
7	10.26	10,500	1.8	0.31	86
8	10.20	17,500	1.6	0.46	92
9	–	12,350	1.9	0.38	89

^{a}Molecular weights were measured with Waters HPLC using Three columns (3, 4 and 5 Å) by using THF as eluent. ^{b}Inherent viscosity was determined by Cannon-Ubbelode viscometer in 1.0 g/dL in DMSO at 20 °C.

marized in Table 3. The chemical structures of the polymers were characterized by NMR and IR spectroscopy and further confirmed by elemental analysis. The polymers obtained here were identified as polyenaryloxynitriles by comparing their IR and NMR spectra with those of model compounds **3-6**. In the IR spectrum, characteristic absorption bands of C≡N, C=C and C-O were exhibited at 2220, 1580, and 1250-1100 cm^{-1}, respectively. The ^{1}H NMR spectrum of polymer **7, 8** and **9** showed multiplets in the range of 6.8-7.2 ppm assignable to aromatic protons of diphenol moiety and a broad singlet peak around 7.6 ppm attributable to the fragment of **2**. On the other hand, the aliphatic units were shown at 1.4 ppm. 1.2-1.8 and 3.8 ppm corresponding to C(CH$_3$)$_2$, -O-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O- and -O-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O-, respectively. These facts indicated that the polyenaryloxynitriles were successfully synthesized via solution polymerization techniques. These spectral observations were consistent with those of model componds. Elemental analyses also supported the formation of the polymers and matched well with the calculated data.

The polyenaryloxyniniles were soluble in several polar aprotic solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and *N,N*-dimehtylacetamide (DMAc), whereas most polymers exhibited no solubility in polar protic solvents such as methanol and ethanol. The polymer **8** derived from 1,5-bis (4-hydroxyphenoxy)pentane showed better solubility than **7** derived from rigid aromatic diol. Higher solubility was associated with the alkyl units, which enhanced a flexibility of the macromolecular chains. The polymers obtained from solution polymerization had inherent viscosity of 0.31-0.46 dL/g. Weight average molecular weights obtained from soluble portion in THF were in the range of 1,1000-18,000. The properties polyenaryloxynitrile including thermal behaviors were already reported in the previous papers.[13]

In conclusion, polyenaryloxynitriles were successfully prepared by solution polymerization from diphenol derivatives and **2** in the presence of DABCO. This method can be also applied to the preparation of poly(enaryloxy-enaminonitriles) by solution polymerization techniques. The kinetic study supported that the nucleophilic vinylic substitution reactions were overall of the third-order, first order each in the vinyl halide, phenol and DABCO, with apparent trend of the improvement of electron donation by the substituent at para-position of phenol derivatives.

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