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We have been studying vinylic nucleophilic substitution as a route to the preparation of novel polymers which exhibit an unusual array of physical properties including excellent solubility in simple, non-aggressive solvents, outstanding thermal stability and relatively high dielectric constants. To improve dielectric and thermomechanical properties as well as to demonstrate the general utility of this synthetic approach, several new bis(chlorovinylidene cyanides) containing biphenyl and terphenyl units have been prepared and polymerized. Thermal and electrical properties of these new materials are discussed.

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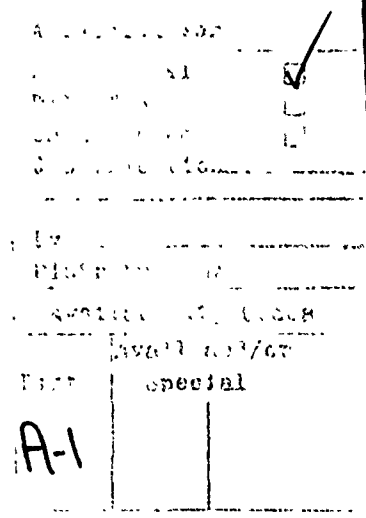

"POLY(ENAMINONITRILES) CONTAINING BIPHENYL AND TERPHENYL RINGS IN THE MAIN CHAIN"

by

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POLY(ENAMINONITRILES) CONTAINING BIPHENYL AND TERPHENYL RINGS IN THE MAIN CHAIN.

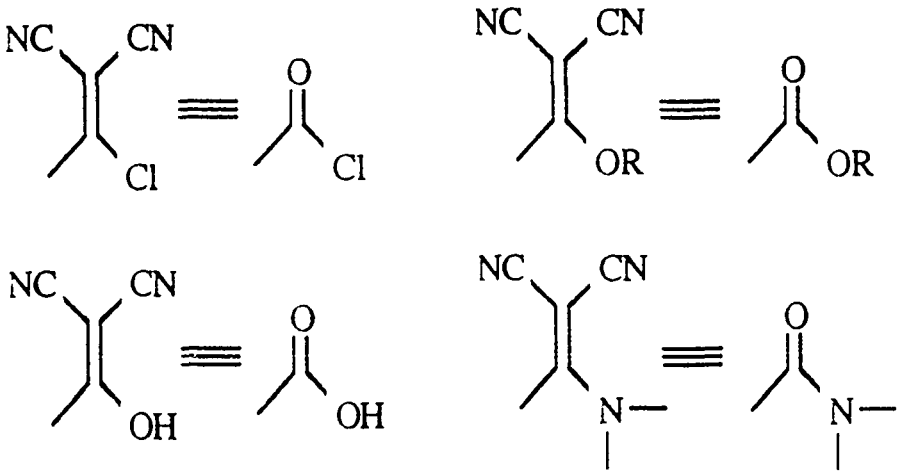
J. A. Moore *, Sang Youl Kim

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180-3590

Abstract: Two new monomers, 4,4'-bis(1-chloro-2,2-dicyano vinyl)biphenyl and 4,4"-bis(1-chloro-2,2-dicyano vinyl)-p-terphenyl, have been synthesized and polymerized with several diamines by vinylic nucleophilic substitution producing poly(enaminonitriles) with molecular weight varying from low to moderately high, depending on the diamines used. The polymers were soluble in polar, aprotic solvents before thermal curing, but became insoluble at high temperatures without the evolution of volatile byproducts. These new polymers exhibit excellent thermal stability, particularly when they contain para-linked aromatic rings. Dielectric measurements of some of the polymers revealed dielectric constants of at least 4.

INTRODUCTION

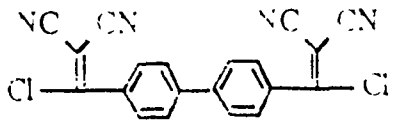
An analogy between dicyanomethylidine and carbonyl groups was pointed out by Wallenfels[1] in 1966. Because of the strong electron withdrawing characteristics of nitrile groups, (the electronegativity of -CN substituted carbon atoms resembles that of N, O, and F atoms), a $C=C(CN)_2$ group may be viewed as the structural equivalent of a carbonyl group. The groups have similar inductive and resonance effects, and have close parallels in many reactions. The following dicyanomethylidine derivatives may also be considered as structurally equivalent to the corresponding carbonyl derivatives.



The application of this analogy in polymerization was not realized until Moore and Robello[2] prepared poly(enaminonitriles) from the bifunctional 1-chloro-2,2-dicyano vinyl monomers with aromatic diamines. The poly(enaminonitrile) from 1,4-bis(1-chloro-2,2-dicyanovinyl) benzene and 4-amino phenyl ether has excellent thermal stability. The advantage of the

enaminonitrile structural unit is that it can be cyclized to an aminoquinoline which makes the cyclized polymer stable and insoluble. Before cyclization, the enaminonitrile group greatly enhances the solubility of the polymer in organic solvents. Another advantage is that poly(enaminonitriles) have good hydrolytic stability (poly(amic acid) is sensitive to hydrolysis). However, the dielectric constant of polymer **1** is about 3. The enaminonitrile group is strongly polarized as reflected in the carbon(^{13}C) nuclear magnetic resonance (NMR) spectrum of the polymer. The difference between the chemical shifts of the carbon atom bearing the amino group and the carbon atom bearing two nitrile groups is approximately 110 ppm.

RESULTS AND DISCUSSION



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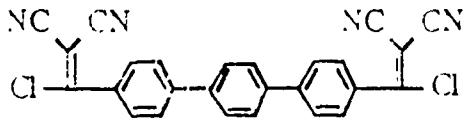

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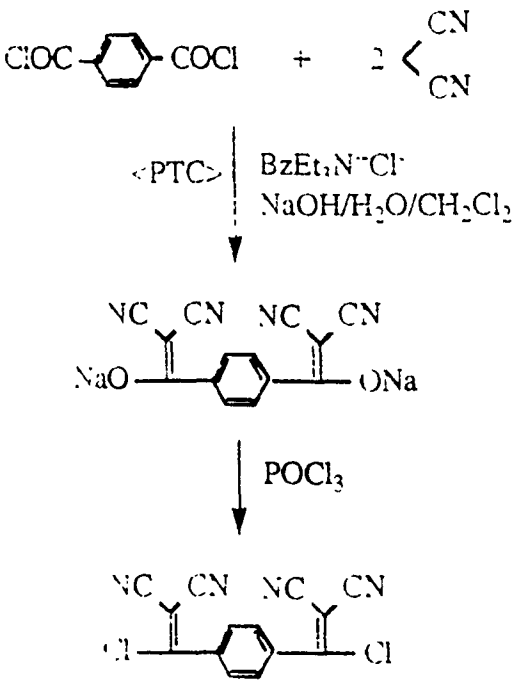
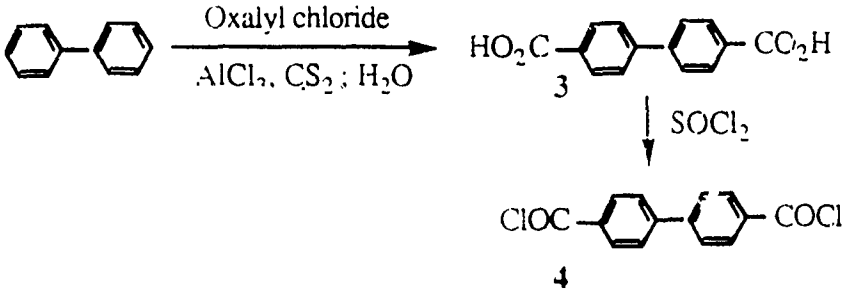
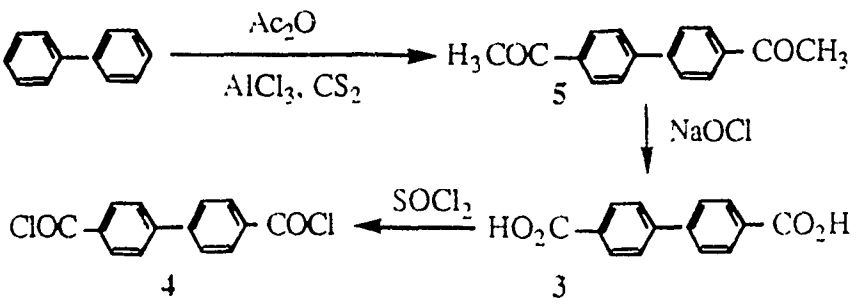
To determine the influence of structural variation on the dielectric behavior of poly(enaminonitriles), it was decided to synthesize monomers containing the biphenyl, **1** and terphenyl, **2**, because control of dielectric constant is a crucial factor for interlayer dielectric applications in VLSI. It is expected that the biphenyl and terphenyl ring in the polymer chains will decrease the dielectric constant of the polymer by diluting the number of polarized enaminonitrile groups in the polymer backbone. The poly (enaminonitriles) derived from biphenyl and terphenyl monomers should also give materials of higher glass transition, enhanced thermal stability, lower water absorption and reduced coefficient of thermal expansion. A previously reported procedure[2] for the preparation of bis(chlorovinylidene cyanides) involves the condensation of malononitrile with terephthaloyl chloride in the presence of a phase transfer catalyst. The precipitated sodium enolate was subsequently chlorinated with phosphorus oxychloride.



The synthesis of the desired monomers thus required the analogous diacid chlorides as starting materials. Biphenyl dicarboxylic acid chloride, **4**, was prepared by Friedel-Crafts reaction of biphenyl with oxalyl chloride and aluminium chloride and subsequent chlorination of the resulting biphenyl diacid, **3**, with thionyl chloride.[4] However, the Friedel-Crafts reaction of biphenyl with oxalyl chloride gave a large amount of ketonic by-products as determined by infrared (IR) spectrometry.

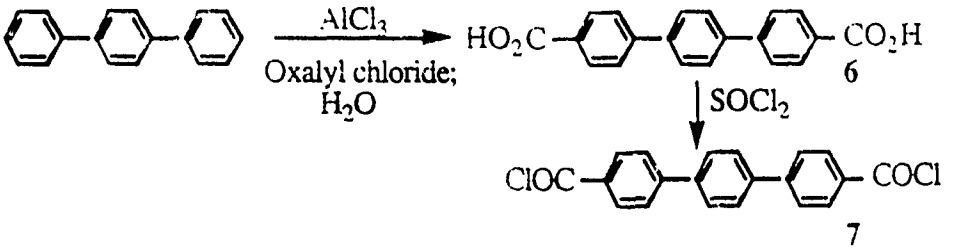


The formation of ketonic by-products was avoided by reacting biphenyl with acetic anhydride. The Friedel-Crafts acylation product, diacetyl biphenyl, **5**, was oxidized to the corresponding diacid with sodium hypochlorite[5] and then converted to the diacid chloride.



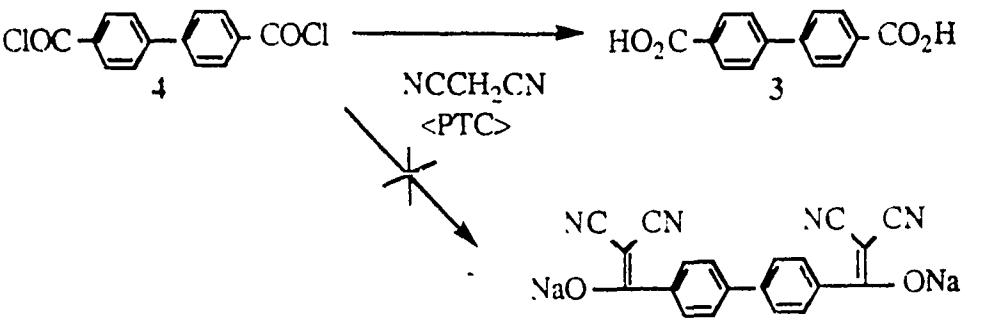
Even though the procedure takes one more step than direct conversion of biphenyl to diphenic acid, the oxidation reaction proceeded almost quantitatively, resulting in a higher total yield.

p-Terphenyl dicarboxylic acid, 6, was prepared from p-terphenyl and oxalyl chloride following modified Friedel-Crafts reaction conditions.[6] The ketonic by-products were removed by recrystallizing terphenyl dicarboxylic acid chloride, 7, twice from benzene.

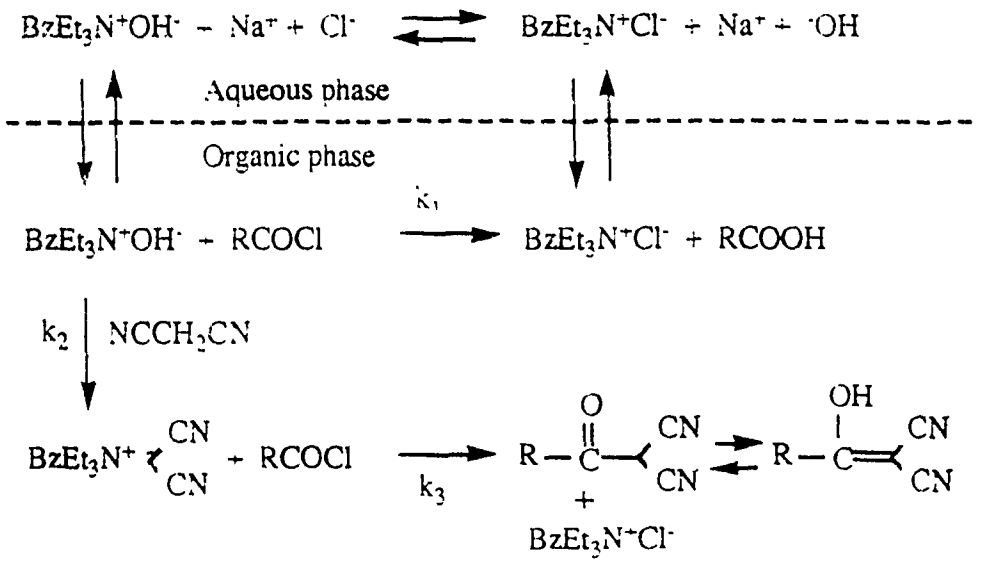


A literature survey revealed that the oxidation of diacetyl p-terphenyl to terphenyl dicarboxylic acid required fairly drastic reaction conditions.[7] It should be noted that p-terphenyl dicarboxylic acid is not soluble in 10% sodium hydroxide solution.[8]

The condensation of biphenyl dicarboxylic acid chloride with malononitrile in the presence of a phase transfer catalyst produced only trace amounts of the desired product (<1%) with biphenyl dicarboxylic acid, 3, as the major product under various reaction conditions.

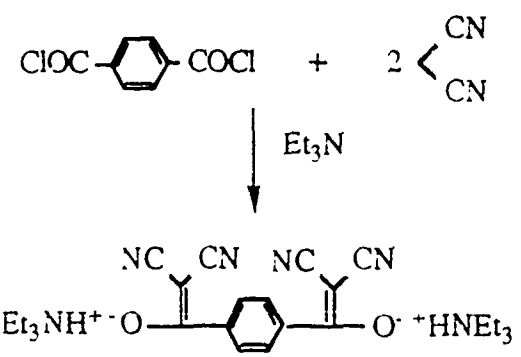


All phase transfer catalyzed reactions involve at least two steps[9]: 1) transfer of one reagent from its normal phase into the second phase and 2) reaction of the transferred reagent with the local reagent. Therefore, condensation of biphenyl diacid chloride with malononitrile under phase transfer catalysis can be formulated as shown in Scheme 1. It is clear from Scheme 1 that hydrolysis of the acid chloride could be a competing reaction and the desired product can be obtained only if k_2 and k_3 are sufficiently larger than k_1. The reaction yields from malononitrile with terephthaloyl chloride and isophthaloyl chloride were 43% and 29%[10], respectively, which indicates that hydrolysis (or other side reactions) occur significantly. Therefore, the unsuccessful attempt with the biphenyl dicarboxylic acid chloride can be attributed to the fact



Scheme 1

that the hydrolysis of biphenyl diacid chloride under these conditions is much faster than the condensation reaction of terephthaloyl chloride with malononitrile. Organic bases should therefore be employed to avoid hydrolysis of the acid chloride. Organic base-catalyzed condensation of acid chlorides with malononitrile was reported by Libis and Fleury[11]. The methyl ammonium salt of bisenol II has been prepared[10], but chlorination of compound II failed. The condensation of biphenyl diacid chloride with malononitrile catalyzed by triethylamine produced a viscous liquid product. The treatment of this product with a mixture of dichloromethane and 5% hydrochloric acid, according to the previous procedure[10], did not give the desired product. Instead, only hydrolyzed biphenyl diacid was obtained. It was thought that a stronger organic base should be used for the biphenyl case because biphenyl diacid chloride is less reactive with malononitrile than is terephthaloyl chloride, probably because the two carbonyl chlorides at the para positions on the same phenyl ring are more



II

efficiently activated than the two acid chlorides connected through two phenyl rings. Several organic bases which have slightly larger pK_a values than malononitrile (see Table 1) were selected and examined in the condensation of biphenyl diacid chloride with malononitrile. The condensation of biphenyl diacid chloride and malononitrile with diisopropyl amine, 1,8-

Diazabicyclo[5.4.0]undec-7-ene (DBU) and Proton Sponge™ gave the desired bis(diisopropyl ammonium) salt, **8**, and the corresponding DBU and Proton Sponge™ salts as a major product. Easy work up and purification of the bis(ammonium) salt prompted the choice of diisopropyl amine as the base for the condensation reaction.

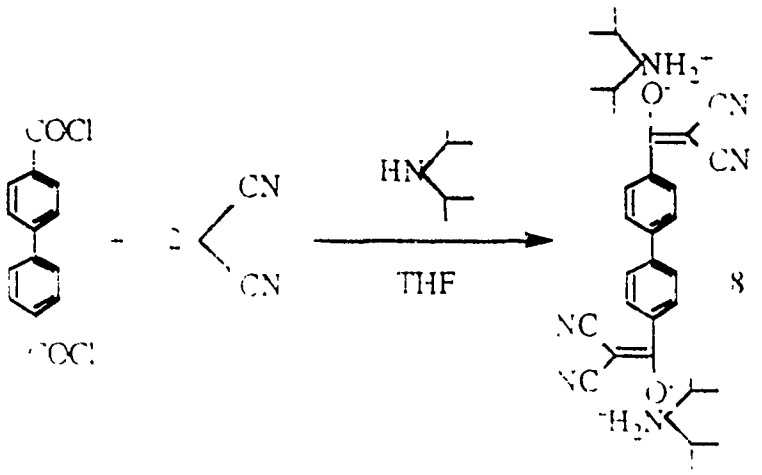


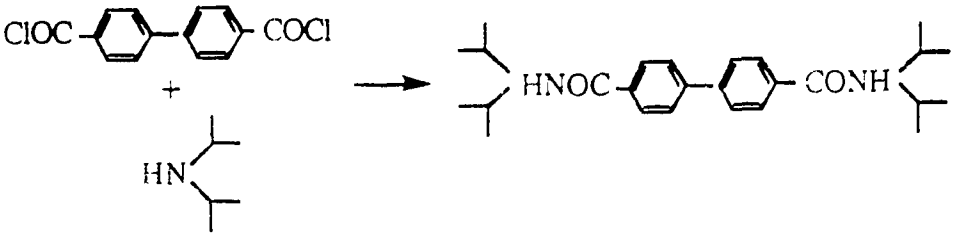
Table 1. pK_a Values of the amines used for the reaction.[12a]

Organic Base	pK_a
Triethyl amine	11.01
Diisopropyl amine	11.13
Pyrrolidine	11.27
DBU*	11.5[12b]
Proton Sponge™**	12.37

*1,8-Diazabicyclo[5.4.0]undec-7-ene.

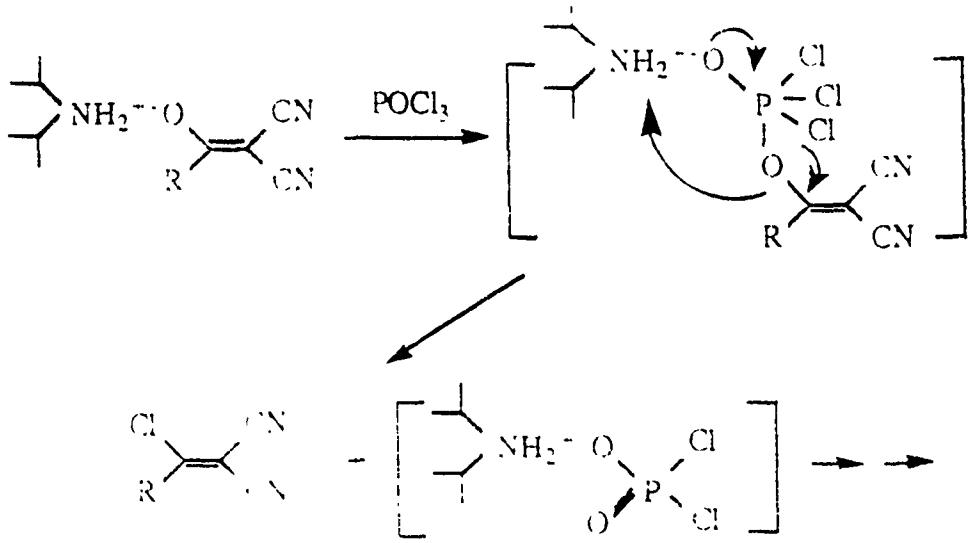
**1,8-Bis(dimethylamino)naphthalene.

It was found later that chlorination of the bis(diisopropyl ammonium) salt (**8**) or the corresponding DBU salt could also be effected without separation of the corresponding amine hydrochloride by-product. The tertiary base, DBU, gave higher yields than did diisopropyl amine, because the secondary amine can form an amide with the acid chloride.

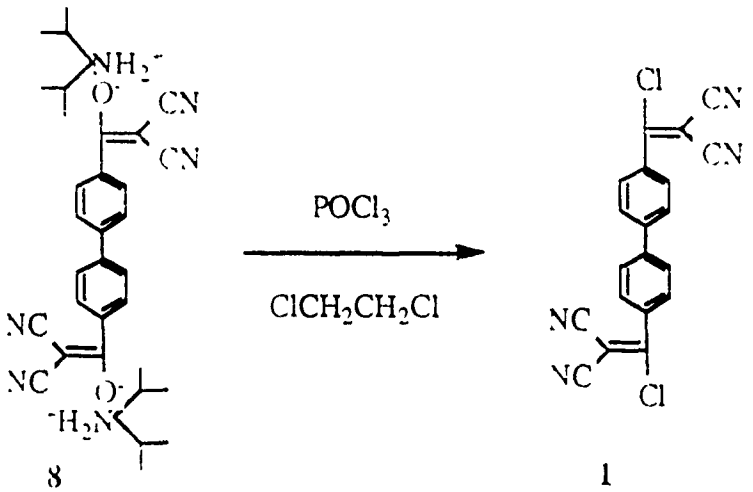


Chlorination of the bis(triethyl ammonium) salt with $SOCl_2$ and PCl_5 was unsuccessful and the difficulty of chlorination was attributed to the ease of expulsion of malononitrile anion from

the postulated intermediate.[10] If the explanation for the failed chlorination is correct, the chlorination with phosphorus oxychloride could avoid the problem. With $POCl_3$, the reaction

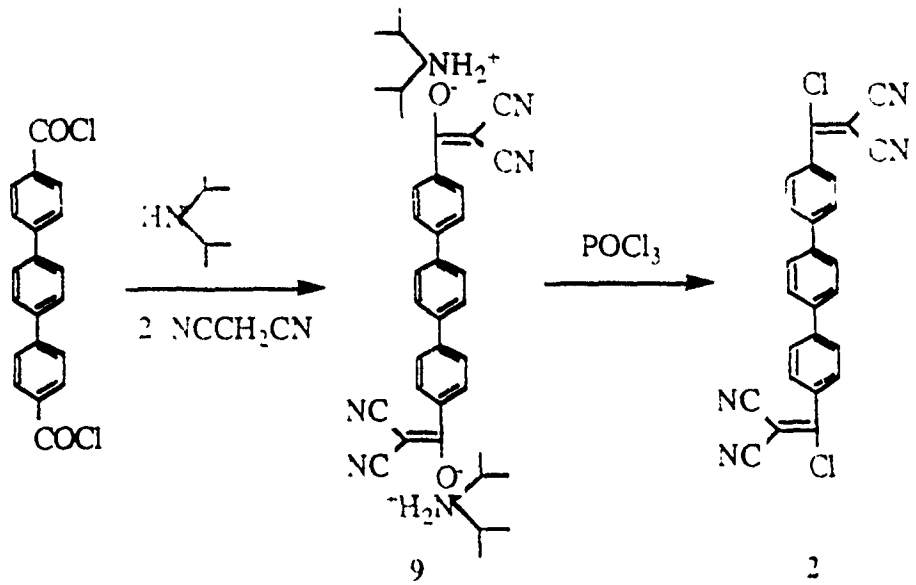


intermediate may not develop negative charge on the carbon atom adjacent to the nitrile groups. The chlorination of bis (diisopropyl ammonium) salt **8** proceeded successfully with phosphorus oxychloride in dichloroethane. The successful chlorination may stem from formation of a stable phosphate salt which is a good leaving group. The chlorination of **8** with oxalyl chloride was unsuccessful.



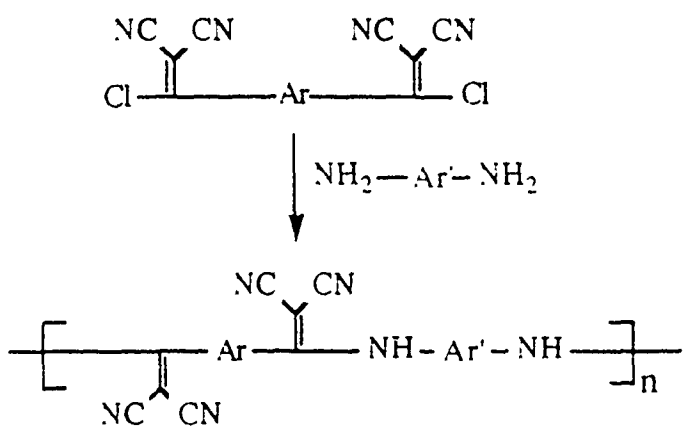
8 **1**

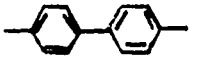
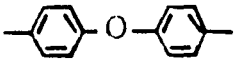
Terphenyl monomer **2** was also prepared by the same procedure. Both monomers were stable solids which could be purified by recrystallization from chlorobenzene and could be stored at room temperature in a desiccator for many weeks without any decomposition.

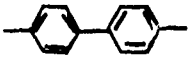
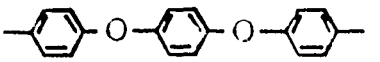


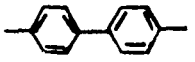
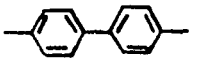
Bis(1-chloro-2,2-dicyanovinyl) monomers **1** and **2** were polymerized with several diamines as shown in Scheme 2 to produce poly(enaminonitriles). In a typical polymerization procedure, equimolar amounts of the bis(1-chloro-2,2-dicyanovinyl) monomer and the diamine were mixed at room temperature in a polar aprotic solvent, N-methyl pyrrolidone (NMP) containing 2% LiCl in the presence of one equivalent of [2.2.2] diazabicyclooctane (DABCO) as an acid acceptor. The mixture turned dark brown and then gradually changed to light brown as polymerization proceeded. The solution was warmed to 75 °C and stirred for 14 hours to complete the reaction. The polymer was precipitated in water and collected by filtration. The polymer was purified by reprecipitation from NMP solution into water. The filtered polymer was washed with deionized water several times and then dried in vacuum at 90 °C for a day. Polymerization of monomer **2** was carried out in a 2 to 1 mixture of NMP and hexamethylphosphoramide (HMPA) containing 2% LiCl.

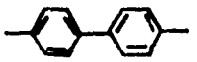
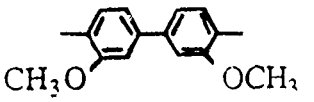
Scheme 2

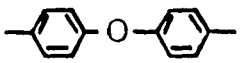


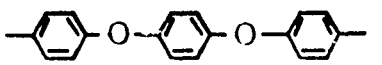
11 Ar =  Ar' = 

12 Ar =  Ar' = 

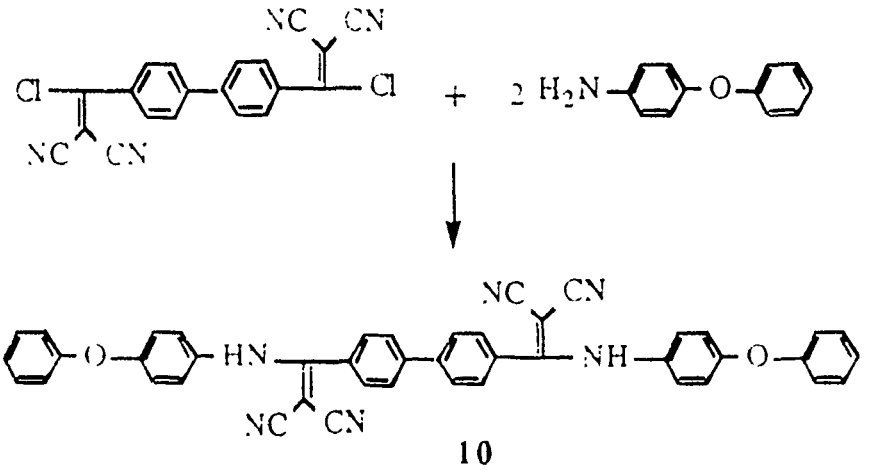
13 Ar =  Ar' = 

14 Ar =  Ar' = 

15 Ar =  Ar' = 

16 Ar =  Ar' = 

The model compound, 4,4'-bis[1-(4-phenoxyphenylamino)-2,2-dicyanovinyl] biphenyl **10**, was also prepared by reacting biphenyl monomer **1** with 4-phenoxy aniline. This model compound represents approximately one and one half repeating units of polymer **11**. The model compound was obtained in very good yield under mild conditions.



10

The spectroscopic data for polymer **11** closely matched those of the model compound **10**. All polymers except **16** were soluble in polar aprotic solvents such as NMP, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) and dimethylsulfoxide (DMSO). Polymer **16** was only soluble in hot DMSO, pyridine and NMP containing LiCl. Fingernail creasable, transparent yellow films were cast from DMF solution except for polymer **13** and **14**. Films of polymer **13** and **14** were somewhat brittle, probably because of relatively low molecular weight of these polymers. In the polymerization of poly(enaminonitrile) **14**, steric hindrance caused by the bulky methoxy group affects the reaction more adversely than the nucleophilic character of the amine is increased by methoxy groups at the 2 and 2' positions. It seems that benzidine, the comonomer of polymer **13**, is the least reactive among the diamines used. The high viscosity of polymer **16**, compared with number average molecular weight (see

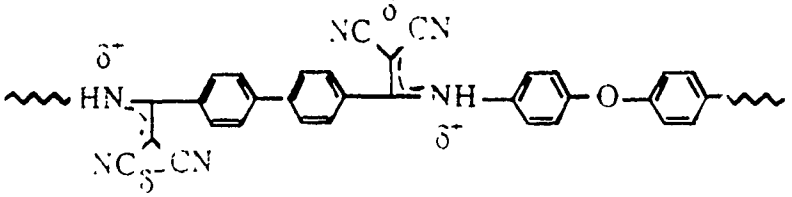
ble 2., may stem from LiCl which increases the polarity of solvent, NMP, and thus olvating power, resulting in a more extended polymer chain in solution.

Table 2. Intrinsic viscosity [η] (in DMF at 25 °C) and molecular weight (M_n) of poly(enaminonitriles) 11, 12, 13, 14, 15 and 16. Molecular weight was obtained from end-group analysis with ^{1}H NMR.

Polymer	[η] (dL/g)	M_n
11	0.38	17.000
12	0.43	20.000
13	0.30	-
14	0.35	-
15	0.42	20.000
16	0.91[a]	25.000

[a] NMP containing 2 % LiCl at 25 °C

mer average molecular weight was calculated from the integral intensity of the ring protons the amine moiety in the polymer chain and the integral intensity of the ring protons of the mine end groups. During the polymerization, a slight excess of amine was added to the ution to prepare poly(enaminonitriles) with amine end groups. This method is possible only the peaks of the aromatic ring protons of the amine end group are not superimposed on the aks from other protons. The peak from amine end groups can be seen clearly at 6.7-6.4 ppm. partial positive charge developed on the enamine nitrogen atom through conjugation with double bond causes a shift of electron density in the adjacent ring. As a result of this effect, peaks of the ring protons of the amine moiety in the polymer chain appeared at lower field, ppm.



THERMAL PROPERTIES

The thermal properties of these polymers were examined by TGA and DSC. Previous work[20] howed that poly(enaminonitriles) could be cyclized without evolution of volatile by-products to a polymer containing some amount of aminoquinoline structures. DSC analysis showed a road exothermic peak for all six poly(enaminonitriles). The maxima of these peaks appeared rom 350 °C to 400 °C depending on the structure of the polymers. When the samples were ooled and rescanned, no exotherms were observed.IR spectra of a film of polymer **11** were aken periodically while the sample was heated at 400 °C in a nitrogen atmosphere. As curing of the polymer proceeds the enamine stretching band at 3260 cm^{-1} disappears and is replaced by two new bands at 3365 cm^{-1} and 3480 cm^{-1} which are characteristic of primary amines. At

ne same time, the intensity of the nitrile band at 2210 cm^{-1} decreases to approximately half compared with the intensity of the nitrile band of the uncured polymer. These changes in IR spectra are consistent with intramolecular cyclization of an enaminonitrile unit to an aminoquinoline structure.

The intramolecular cyclization was also reflected in the DSC curves where the maximum exothermic peak appeared at different temperatures depending on the structure of the amine comonomer (see Table 3).

Table 3. Exothermic peak temperature and T_g of poly(enaminonitriles) observed by DSC.

Polymer	Exothermic Peak Temperature (°C)	T_g (°C)
11	350	220
12	350	-
13	370	325*
14	350	-
15	360	240
16	355	-

* After curing.

Poly(enaminonitriles) **11**, **12**, **14**, **15** and **16** from amines bearing electron donating groups showed the maximum exotherm around 350 °C. The polymer from benzidine, which does not have any electron donating or withdrawing group on the ring, showed a maximum at 370 °C. These results support the proposal that the rearrangement reaction occurs through electrophilic aromatic substitution (arenium-ion mechanism)[13] In this mechanism, electron donating groups stabilize the intermediates, while electron withdrawing groups which increase a positive charge on the ring destabilize the intermediates.

Thermogravimetric analysis of the six polymers in air and under nitrogen showed that the polymers have excellent thermal stability.Structural effects on the thermal stability are clearly reflected: better thermal stability is obtained the more para-linked aromatic rings are in the polymer chain.

The thermal stability of six polymers **11**, **12**, **13**, **14**, **15** and **16** is summarized in Table 4. The temperature at which 10% weight loss of polymers **15** and **16** with more para-linked aromatic rings in the chain is higher than for polymers **11** and **12**. The 10% weight loss temperatures of polymer **11** and **12** indicate the effect of flexible linking groups on thermal stability of polymers. Polymer **12**, which has two ether linkages, was less stable in air and nitrogen than polymer **11** which has only one ether linkage in the repeating unit. Polymer **14**, which has methoxy groups on the aromatic rings, showed the least thermal stability among these six polymers. Generally, replacement of hydrogen by other atoms except fluorine results in reduced thermal stability. At elevated temperature in an oxidizing atmosphere, hydrogen substituents themselves become reactive. In air, polymer **11** has a higher 10% weight loss temperature than does polymer **13**, even though polymer **13** exhibited better thermal stability

under nitrogen. This apparently conflicting result may stem from the molecular weight of the polymers, which has more effect in air than in nitrogen. Intrinsic viscosities of polymer **11** and **13** are 0.38 dL/g and 0.30 dL/g, respectively.

Table 4. Weight Loss of Poly(enaminonitriles) in TGA.

Polymer	10% Weight Loss Temperature in N_2	10% Weight Loss Temperature in air	Residual Weight % at 900 °C in N_2
11	600 °C	530 °C	81
12	520 °C	500 °C	73
13	610 °C	500 °C	77
14	470 °C	450 °C	71
15	640 °C	570 °C	84
16	550 °C	545 °C	80

DIELECTRIC PROPERTIES

It was reported earlier[3] that poly(enaminonitrile) I had a dielectric constant greater than 5 which is large compared with that of a corresponding polyimide and this high dielectric constant was attributed to the presence of the strongly polarized enaminonitrile group. Poly(enaminonitriles) from biphenyl monomer **1** and terphenyl monomer **2** should exhibit lower dielectric constants than polymer XII. Dielectric constants of these polymers were measured with mercury electrodes using an HP 4274A LCR meter at room temperature. The frequency range was 0.1 to 100 KHz. The films had been cast from DMF solution. The results are shown in Table 5 to 8. The dielectric constant of poly(enaminonitriles) **11**, **12**, **13** and **14** at 100 KHz were 4.95, 3.94, 4.53 and 4.04, respectively. These values are smaller than the dielectric constant of poly(enaminonitrile) XII. These results clearly show the dipole dilution effect on dielectric constant of the polymer. A bulky monomer lowers the number of strongly polarized enaminonitrile groups per unit volume.

Table 5. Dielectric measurement for poly(enaminonitrile) **11**. The film thickness was 17.9 μm. After the initial measurement, the film was soaked in boiling water for 3 hours, and then redried in vacuum at 110 °C for 3 days

Frequency	Before being soaked in water		After being soaked in water		After being redried in vacuum	
(KHz)	ε	tan δ	ε	tan δ	ε	tan δ
0.1	5.19	0.0124	5.88	0.0143	5.10	0.0093
0.2	5.16	0.0116	5.84	0.0132	5.09	0.0089
0.4	5.14	0.0105	5.81	0.0119	5.06	0.0082
1	5.10	0.0097	5.77	0.0110	5.03	0.0080
2	5.08	0.0093	5.75	0.0104	5.01	0.0079
4	5.06	0.0091	5.72	0.0099	5.00	0.0079
10	5.04	0.0097	5.69	0.0100	4.97	0.0087
20	5.01	0.0106	5.66	0.0103	4.95	0.0095
40	4.98	0.0120	5.64	0.0108	4.93	0.0107
100	4.95	0.0141	5.60	0.0117	4.89	0.0120

Table 6. Dielectric measurement for poly(enaminonitrile) **12**. The film thickness was 14.1 μm. After the initial measurement, the film was soaked in boiling water for 3 hours.

Frequency	Before being soaked in water		After being soaked in water	
(KHz)	ε	tan δ	ε	tan δ
0.1	4.08	0.0085	4.53	0.0096
0.2	4.07	0.0080	4.51	0.0091
0.4	4.06	0.0072	4.50	0.0083
1	4.04	0.0068	4.47	0.0079
2	4.03	0.0066	4.46	0.0076
4	4.02	0.0066	4.44	0.0074
10	4.00	0.0073	4.42	0.0079
20	3.99	0.0083	4.41	0.0084
40	3.97	0.0096	4.39	0.0093
100	3.94	0.0117	4.36	0.0108

Table 7. Dielectric measurement for poly(enaminonitrile) **13**. The film thickness was 7.5 µm. After the initial measurement, the film was soaked in boiling water for 3 hours, and then redried in vacuum at 110 °C for 3 days.

Frequency (KHz)	Before being soaked in water		After being soaked in water		After being redried in vacuum	
	ε	tan δ	ε	tan δ	ε	tan δ
0.1	4.77	0.0148	6.03	0.0423	4.93	0.0124
0.2	4.74	0.0136	5.94	0.0346	4.90	0.0116
0.4	4.72	0.0122	5.87	0.0288	4.88	0.0106
1	4.68	0.0112	5.78	0.0236	4.85	0.0100
2	4.66	0.0106	5.73	0.0207	4.83	0.0096
4	4.64	0.0104	5.69	0.0186	4.81	0.0094
10	4.61	0.0108	5.63	0.0169	4.78	0.0098
20	4.59	0.0115	5.59	0.0160	4.76	0.0102
40	4.57	0.0126	5.55	0.0154	4.74	0.0107
100	4.53	0.0145	5.50	0.0150	4.70	0.0109

Table 8. Dielectric measurement for poly(enaminonitrile) **14**. The film thickness was 5.6 µm.

Frequency (KHz)	Capacitance F x 10^{11})	ε	tan δ
0.1	69.37	4.29	0.0197
0.2	68.83	4.26	0.0175
0.4	68.37	4.23	0.0153
1	67.76	4.19	0.0135
2	67.40	4.17	0.0123
4	67.08	4.15	0.0116
10	66.61	4.12	0.0113
20	66.29	4.10	0.0115
40	65.96	4.08	0.0118
100	65.40	4.04	0.0120

A dipole moment of 4.21 D was calculated for the following enaminonitrile when the amino group was coplanar with the double bond.[14]

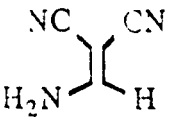


Table 9 contains dielectric data of four poly(enaminonitriles) and the volume of the repeating unit of each polymer. The volume was calculated from group contribution parameters[15]. Even though the dielectric constant is not directly proportional to the volume of the repeating unit, the data show that the larger the repeating unit volume, the lower the dielectric constant. Polymers **14** and **12** have very small differences in dielectric constants compared to the difference of repeating unit volumes. This result could be caused by the bulky methoxy group which occupies volume without contributing significantly to the net dipole moment of the molecule and forces the large dicyano groups off the same side of the molecule, resulting in a reduction of the net dipole moment.[16] Polymer **13** has a lower dielectric constant than polymer **11** which has a larger repeating unit volume. This discrepancy may be the result of absence of the ether linkage, resulting in more rigid structure which makes orientation of the polar groups more difficult. The oxygen atom also affects the net dipole moment.

Table 9. Repeating unit volume and dielectric constant of poly(enaminonitriles)

Polymer	Volume of Repeating Unit* (cm^3/mol)	Dielectric Constant at 100 KHz
12	449	3.94
14	419	4.04
11	373	4.95
13	363	4.53

* Calculated from group contribution parameter[15].

Electronic, atomic and orientation polarization are all caused by charges that are locally bound in atoms, molecules or the structure of solids. Another type of polarization in the bulk sample, the so called interfacial polarization, can occur when the sample contains defects or a separated phase.[17] The separated phases cause a localized accumulation of charge at the interfaces which increases the dipole moment , resulting in unusually high values of dielectric constant at low frequency. Interfacial polarization principally influences the low frequency (10^{-5} to 10^{2} Hz) dielectric properties and decreases as frequency increases. The dielectric data of polymers **11**,**12**, **13** and **14** did not show the phenomenon expected from interfacial polarization.

Orientation polarization is a relatively slow process compared with electronic and atomic polarization. Dielectric relaxation is the lag in dipole orientation behind an alternating electric field. Under the influence of such a field, the polar molecules of the system rotate toward an equilibrium distribution in molecular orientation with a corresponding dielectric polarization.[18] When the polar molecules are very large or the viscosity of the medium is very high, the rotating motions of the molecules are not sufficiently rapid for the attainment of equilibrium

with the field. The polarization then acquires a component out of phase with the field, and the displacement current acquires a conductance component in phase with the field, resulting in dielectric loss which is usually a thermal dissipation of energy. The complex dielectric constant[19] of the dielectric material is expressed as $\varepsilon^* = \varepsilon' - i\varepsilon''$ where ε' is the measured dielectric constant of the sample and ε'' is the imaginary part of the dielectric constant, known as the dielectric loss factor. The ratio of ε' and ε'' is called tan δ.

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\text{energy dissipated per cycle}}{\text{energy stored per cycle}}$$

Tan δ is usually called the dielectric loss tangent or the dissipation factor. The dielectric constant and dielectric loss at high frequency are characteristics of the chemical structure of the polymer. Tan δ becomes increasingly sensitive to small molecules such as residual solvent, water or impurities in polymer films at low frequency. If there is a significant amount of residual solvent or ionic impurities such as LiCl, tan δ would be high at low frequency and much lower at high frequencies. As shown in Table 5, 6, 7 and 8, tan δ for polymer **11**, **12**, 13 and **14** changes very little over the whole frequency range examined, indicating the polymer samples were free of any significant amount of impurities. However, it was found that the ε and the dissipation factor of polymer **11** and **13** decreased slightly (see Table 5 and 7) when the films which were soaked in boiling water for 3 hours were redried in vacuum at 110 °C for 3 days. This observation may be an indication that the films contained a small amount of ionic species, probably LiCl which was used to increase solubility during the polymerization, and the ionic impurities were diffused out when the films were soaked in water.

To determine the effect of absorbed water on the dielectric properties, the polymer films were boiled in water for 3 hours and subjected to dielectric measurement (see Table 5, 6 and 7). As expected, the dielectric constants of the polymers increased after soaking in boiling water. It is interesting that polymer **13** absorbed less water than polymer **11** (see Table 10), while the change in dielectric constant after soaking in boiling water is much larger than in polymer **11**. This result may stem from the absorbed water in the film **13** which acts like a plasticizer making the very rigid polymer chain more mobile, resulting in greater orientation of the polarized enaminonitrile group.

The dissipation factor of the dried film fluctuated very little over the frequency range used. After the films were soaked in water, tan δ data of polymer **13** showed the characteristic changes caused by absorbed water: tan δ rapidly decreased as frequency increased. However, tan δ of polymer **11** and **12** were almost constant over the frequency range examined. It may stem from the interaction of the absorbed water in polymer **11** and **12** with oxygen atoms (ether linkage) and enaminonitrile groups, which affects the relaxation time of the absorbed water molecule. Further investigation of the change in tan δ over a wider range of frequency and temperature is needed to understand these phenomena.

Table 10. Water absorption and dielectric constant change of poly(enaminonitriles).

Polymer	Water Absorption (%)	Dielectric Constant Change (%) at 100 KHz
11	3.17	13.3
12	2.41	11.0
13	2.24	26.4

CONCLUSIONS

Two new monomers, **1** and **2**, have been synthesized and polymerized with several diamines, producing poly(enaminonitriles) with molecular weights varing from low to moderately high, depending on the diamine comonomers. The polymers, except **16**, were soluble in polar, aprotic solvents such as NMP, DMF, DMAc and DMSO before curing, but became insoluble in any organic solvents after curing. Polymer **16** was only soluble in hot DMSO, pyridine and NMP containing 2% LiCl. Tough films were cast from DMF solutions of polymer **11, 12, 15** and **16**. The films of polymers **13** and **14** were somewhat brittle.

These poly(enaminonitriles) undergo curing at 350 - 400 °C without formation of volatile by-products. Maximum exothermic peak temperatures due to curing varied with the diamine structure: electron donating substituents on the aromatic ring decreased the curing temperature. Poly(enaminonitriles) from biphenyl and terphenyl monomers with aromatic diamines which do not have side groups on the aromatic ring have excellent thermal stability. Polymers with more para-linked aromatic rings in the polymer chain have better thermal stability. Side groups, such as methoxy attached to the aromatic ring reduced the thermal stability of the polymer. The dielectric constants of polymers **11, 12, 13,** and **14** were found to be 4.95, 3.94, 4.53 and 4.04 at 100 KHz, respectively. The dielectric constants of poly(enaminonitriles) depend on the volume of the repeating unit and the number of polar atoms such as oxygen in the polymer chain. A polymer with larger repeating unit volumes has a lower dielectric constant because the strongly polarized enaminonitrile group is more diluted. When the two poly(enaminonitriles) have similar repeating unit volumes, the polymer without polar atoms in the chain exhibited a lower dielectric constant than the polymer with polar atoms.

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