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# Synthesis and Characterization of Polyamides Derived From Cyano-Containing 1,4-Bis(4-aminophenoxy)-benzene Monomers

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## Summary

A series of potentially electroactive aromatic-aliphatic polyamides based upon 3,6-bis(2-cyano-4-aminophenoxy)phthalonitrile (**1**) was synthesized in N,N-dimethylacetamide to yield polymers with intrinsic viscosities of 0.66-1.04 dL/g. One polyamide was synthesized using 1,4-bis(2-cyano-4-aminophenoxy)benzene (**2**) to compare to **1**. There appears to be an odd-even effect of methylene spacer length upon the mechanical properties and glass transition temperature, with an even number of methylene groups yielding the larger values. Thermogravimetric analysis in air and nitrogen showed that these polymers had similar 5% weight losses in both atmospheres, which indicated that oxygen is not involved in the initial degradation of these polymers.

## Introduction

The field of piezoelectric polymers began with the finding that poly(vinylidene fluoride) (PVDF) displays a high piezoelectric response when drawn and poled [1]. The ability of dipoles to orient along the electric field is the source of the piezoelectric response. Since then there have been studies of many other polymer structures, such as polyamides [2-5], polyurethanes [6,7], polyureas [8,9] and poly(vinylidene cyanide)s [10,11].

Scheinbeim and coworkers have extensively studied odd-numbered nylons, which demonstrated ferroelectric switching [2,3]. X-ray analyses have shown that odd-numbered nylons form hydrogen bonded sheets that lie parallel to the film surface. When an electric field is applied there are 90º rotations of the NH and CO dipoles, resulting in hydrogen bonded sheets aligned perpendicular to the film surface. Remanent polarization ($P_r$) values of nylons are high, with nylon 5 having a $P_r$ of 125 mC/m$^2$. Whereas PVDF starts to lose polarization at 80 ºC, nylons have higher thermal stabilities due to the intermolecular hydrogen bonding. It has been theorized that nylon 5 maintains polarization until approximately 250 ºC [2].

Amorphous polyamides containing aromatic units have also displayed ferroelectric responses. Koizumi and coworkers have studied polymers and copolymers containing isophthaloyl and terephthaloyl groups with various methylene length spacers [4]. Although incorporation of ring systems into polyamides lowered the $P_r$ values relative to pure nylons, $P_r$ values up to 67 mC/m$^2$ could be achieved. Polarized IR spectroscopy also showed that the NH and CO dipoles oriented along the electric field during poling. Also, intermolecular hydrogen bonding was shown to exist, which allowed for retention of dipole orientation up to the glass transition temperature ($T_g$) [4].

The odd-even trend in $P_r$ values was not seen in a series of polyamides obtained from *m*-xylylenediamine and aliphatic dicarboxylic acids [5]. In general, the trend followed that, as the methylene spacer length decreased from 13 to 6 units, the $P_r$ increased. X-ray analysis of the polymer from *m*-xylylenediamine and pimelic acid revealed that the amide groups were packed antiparallel to each other, similar to that of nylon 6,6 and nylon 6,10. It was speculated that the degree of crystallinity was responsible for the $P_r$ values, with easier dipole orientation in the amorphous regions of the polymer.

The focus of this work is aromatic-aliphatic polyamides derived from cyano-containing 1,4-bis(4-aminophenoxy)benzene monomers. It was believed that intermolecular hydrogen bonding could stabilize the dipole orientation after poling. Besides the NH and CO dipoles of the amide, the cyano group would also contribute to the degree of orientation. The thermal and mechanical properties are disclosed in this initial publication. These data are directly tied to the piezoelectric properties of polymers, which will be the focus of subsequent publications.

## Experimental Section

### *Materials*

All diamines were prepared according to the literature [12]. Diacid chlorides were prepared from respective diacids through a reaction with thionyl chloride. Diacid chlorides were distilled under vacuum prior to use. Trimethylsilyl chloride was distilled from calcium hydride. N,N-Dimethylacetamide (DMAc) was distilled from phosphorus pentoxide.

### *Characterization*

Thermogravimetric analyses (TGA) were performed in nitrogen and air (flow rate = 50 mL/min) at a heating rate of 2.5 ºC /min using a Perkin Elmer Pyris Diamond TG/DTA Thermogravimetric/Differential Thermal Analyzer. Thermomechanical analyses (TMA) were performed at 5 ºC/min on polymer films under a static force of 25 mN using a Perkin Elmer TMA7 Thermomechanical Analyzer with Thermal Analysis Controller TAC 7/DX. The $T_g$s were determined by TMA as the point of inflection from the baseline. Intrinsic viscosities were determined with a Cannon-Ubbelohde #100 viscometer. Flow times were recorded for N-methyl-2-pyrrolidinone solutions with polymer concentrations of approximately 0.50 g/dL to 0.25 g/dL at 25.0 ± 0.1 ºC. Mechanical properties of thin films were determined on a Sintech 2W instron according to ASTM D882 at a strain rate of 0.51 cm/min (0.20 in/min).

### *Dielectric Characterization*

Polymer films were dried at 90 ºC under vacuum overnight prior to application of gold electrodes. Gold electrodes were sputtered onto both sides of polymer films. Electrode thicknesses were approximately 40 nm thick. Measurements were performed using Novocontrol Broadband Dielectric Converter BDC and Impedance/Gain-Phase Analyzer Solartron SI 1260 equipped with Novocool. Analyses were performed at 2 ºC/min to 240 ºC, then cooled at 2 ºC/min to room temperature. The $T_g$s were determined at the peak of the dielectric losses. All $T_g$s were determined during the second heating.

### *General Polymerization*

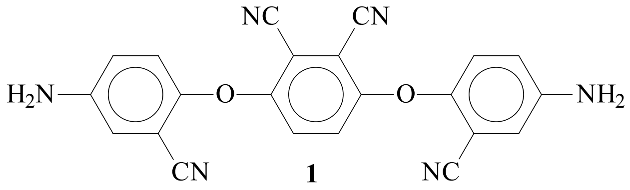
To a 100 mL, three-neck, round bottom flask equipped with an overhead stirrer, nitrogen inlet, and nitrogen outlet were added diamine (4.4 mmol) and DMAc (10 mL). After the diamine dissolved, the flask was cooled with a dry ice/brine bath. To the solution was added trimethylsilyl chloride (0.8 eq/diamine). After 15 min the cooling bath was removed and the solution was allowed to warm to room temperature. The solution was allowed to stir at room temperature for 30 min. The flask was cooled with a dry ice/brine bath for 15 min. To the solution were added diacid chloride (4.4 mmol) and DMAc (total reaction concentration 15% wt/V). The solution was allowed to warm to room temperature overnight as the cooling bath was allowed to warm overnight. The viscous solution was poured into stirring methanol causing a tan, fibrous polymer to precipitate. The polymer was collected by filtration, and then dried at 100 ºC under vacuum overnight. A 20% (wt/V) solution in N,N-dimethylformamide was prepared and pressure filtered through nylon filter paper (0.8-1.2 μm pore size, depending upon polymer solution viscosity). Films were cast in a clean room and dried at 150 ºC under nitrogen. After the removal of films from the glass plates, the films were dried at elevated temperatures under vacuum to remove remaining solvent and water, affording yellow to amber-colored transparent films. Film thicknesses ranged from 13 to 23 μm.

## **Results and Discussion**

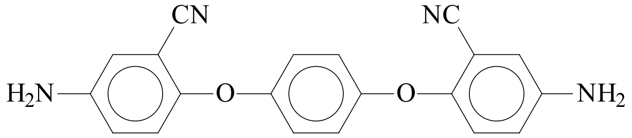
Polyamides prepared from **1** (figure 1) were synthesized with a series of aliphatic diacid chlorides that vary the methylene spacer lengths, and one polyamide was synthesized from **2**. Through a comparison of polyamides from monomers **1** and **2** with the same diacid chloride, the effect of cyano-group density on the properties can be determined.

Monomer **1** was polymerized with diacid chlorides with methylene spacer lengths ranging from 4 to 8. Since it is well-known that the physical properties of polymers vary depending upon whether there is an odd number or even number of methylene groups, it was speculated that the properties of these polyamides may also have an odd-even dependence. In the case of these polymers, an even number of methylene groups should allow the polymers to have more effective hydrogen bonding than when there are an odd number of methylene groups (figure 2). Such effective hydrogen bonding may allow for better retention of dipole alignment after poling compared to non-effective hydrogen bonding, as with odd-numbered methylene spacers.

Polyamides were prepared from monomer **2** (figure 1) through a reaction with a diacid chloride at reduced temperature in DMAc. Attempted polymerizations of **1** with aliphatic diacid chlorides using the same procedure as for monomer **2** led to low molecular weight powders. The addition of 0.8 equivalents of trimethylsilyl chloride to **1** before addition of the diacid chlorides led to high molecular weight polymers, as evidenced by the fibrous nature of the precipitated polymers, as well as high intrinsic viscosities. It is believed that the presence of the phthalonitrile ring system in the middle ring of structure **1** withdraws more electron density from the amino groups than the benzene ring system in the middle ring of structure **2**. This decrease in

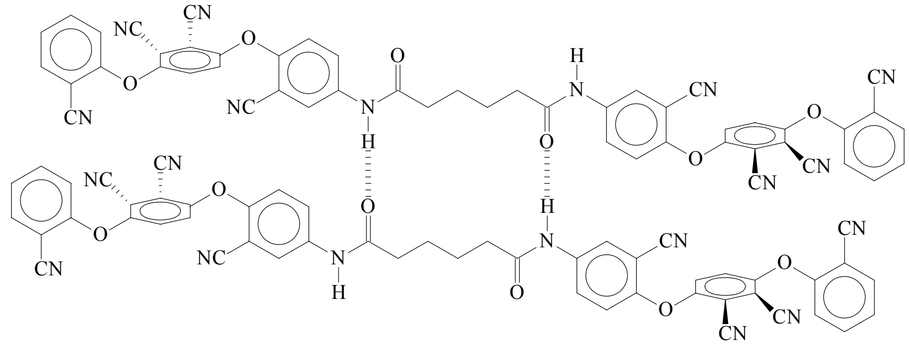


**1**

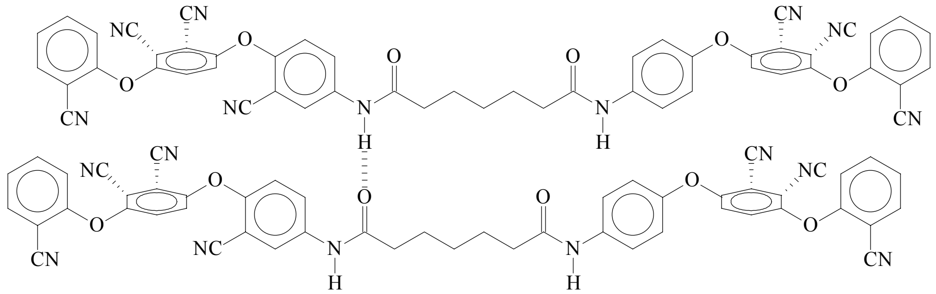


**2**

**Figure 1.** Structures of cyano-containing monomers



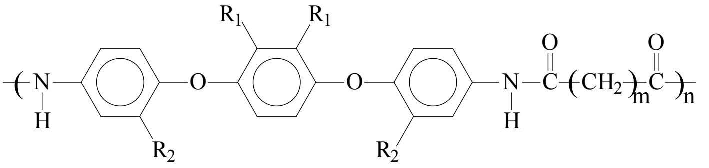
Even number of methylene groups



Odd number of methylene groups

**Figure 2.** Even vs. odd methylene spacer repeat group alignment

electron density would lead to a less reactive diamine, which is why the reactivity of the amino groups needs to be increased in order to synthesize high molecular weight polyamides. Evidently the cyano groups *meta* to the amino groups does not withdraw much electron density from the amino groups, as evidenced by the ability of **2** to synthesize high molecular weight polymer without requiring the amino groups to have increased activity through addition of trimethylsilyl chloride.
The thermal properties of the polymers are listed in Table 1. The 5% weight losses ranged from 325 to 358 °C. The low thermal stability is due to the C-C and C-H bonds in the aliphatic portion of the polymer, which are known to possess lower bond dissociation energies than the aromatic C-C and C-H bonds. In all cases except for the polyamide from **2**, the 5% weight losses were nearly identical in each series in both nitrogen and air. The polyamide from **2** has a slightly higher decomposition temperature in nitrogen than in air. The similar decomposition temperatures in air and nitrogen indicate that the decomposition pathway is not a thermo-oxidative process in the initial stages of polymer decomposition. Decomposition would initially involve the aliphatic portions of the polymer chains due to the relatively weak carbon-carbon single bonds, which are easier to dissociate than amide N-C bonds or aromatic C-C bonds. Therefore it is unlikely that the thermal stability of the polyamide from **2** would be any different than from **1** in the initial stages of polymer degradation.



**1**: $R_1$=$R_2$=CN
**2**: $R_1$=H, $R_2$=CN

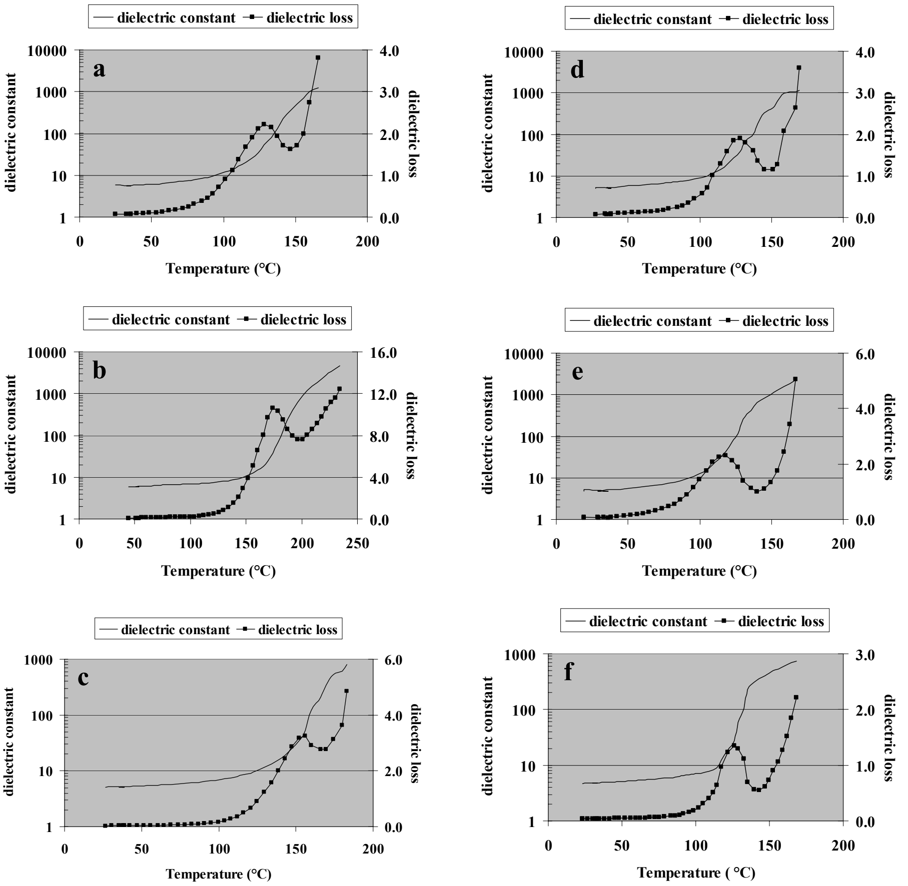
**Table 1.** Thermal properties of polyamides

| Diamine | m | [ η ] (dL/g)[1] | $T_g$ (°C)[2] | $T_g$ (°C)[3] | $T_d$, air (°C)[4] | $T_d$, $N_2$ (°C)[4] |
|---|---|---|---|---|---|---|
| 1 | 4 | 1.04 | 182 | 185 | 356 | 353 |
| 1 | 5 | 0.66 | 174 | 183 | 355 | 350 |
| 1 | 6 | 0.77 | 175 | 159 | 353 | 343 |
| 1 | 7 | 0.77 | 159 | 151 | 340 | 340 |
| 2 | 7 | 0.89 | 139 | 123 | 340 | 358 |
| 1 | 8 | 1.04 | 159 | 161 | 325 | 333 |

1 Intrinsic viscosity determined in N-methyl-2-pyrrolidinone at 25.0 ± 0.1 °C
2 Determined by dielectric spectroscopy at 0.3 Hz at a heating rate of 2 °C/min
3 Determined by TMA at a heating rate of 5 °C/min with a static force of 25 mN
4 Temperature at which polymer underwent 5% weight loss by TGA at a heating rate of 10 °C/min

The $T_g$s of the polyamides decreases as the methylene spacer length increases. The dielectric spectroscopic analyses (figure 3) and TMA (figure 4) showed similar trends in this behavior. The dielectric measurements are a more accurate measure of the $T_g$ than TMA. The $T_g$ by TMA (extension) is more of a softening point, the point where the curve deviates from the baseline upon heating the polymer. The $T_g$ of the polyamide from **2** is lower than its analog with **1**. This indicates that the two cyano groups in the phthalonitrile portion of the ring in **1** hinder rotation of the two other aromatic rings in the system due to steric hindrance with the other cyano groups. Since the polyamide from **2** has aromatic C-H units in the middle ring instead of aromatic C-CN units, the steric hindrance is much less. Thus, the $T_g$ of polyamides from **2** will be lower than polyamides from **1**.

The tensile properties of the polymers are listed in Table 2. There appears to be an odd-even dependence on the tensile strength and tensile modulus of the polymer (figure 5). When the aliphatic portion is long (m=8), the trend is no longer observed. Both the tensile strength and tensile modulus are higher in m=4 and 6 than when m=5 and 7. This may be due to intermolecular hydrogen bonding (figure 2) in which there is more effective hydrogen bonding in the case with m=even number than when m=odd number. Another possibility is that the polymers with m=even number have a higher degree of crystallinity than those with m=odd number. Standard differential scanning calorimetry experiments did not reveal any thermal behavior indicative of a $T_g$, crystallization, or melting. These polyamides will need to be analyzed by x-ray diffraction to determine if any crystallinity or phase separation exists in the polymers.



**Figures 3a-3f.** Dielectric spectra at 0.3 Hz of (a) **1**/$(CH_2)_4$, (b) **1**/$(CH_2)_5$, (c) **1**/$(CH_2)_6$, (d) **1**/$(CH_2)_7$, (e) **1**/$(CH_2)_8$, and (f) **2**/$(CH_2)_7$

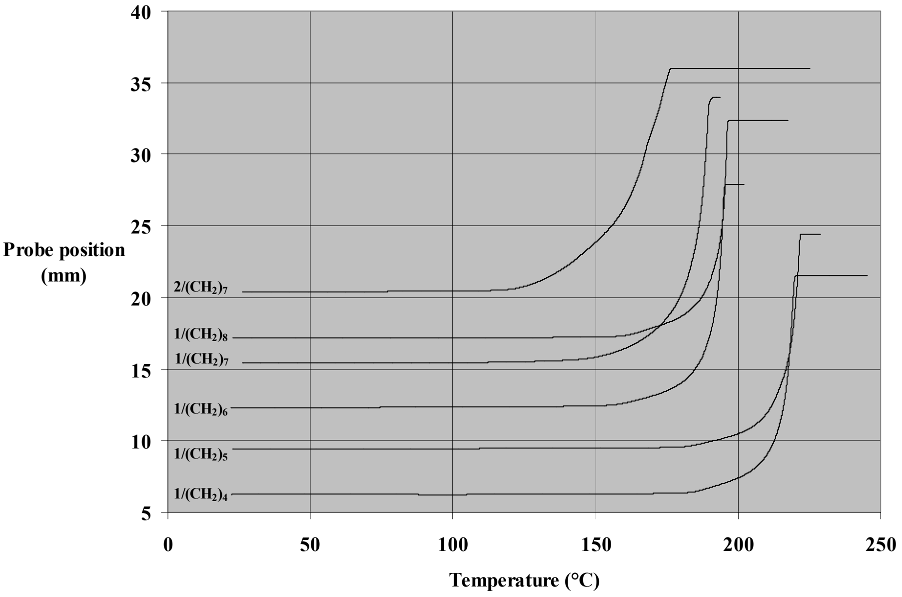


**Figure 4.** TMA thermograms of polyamides

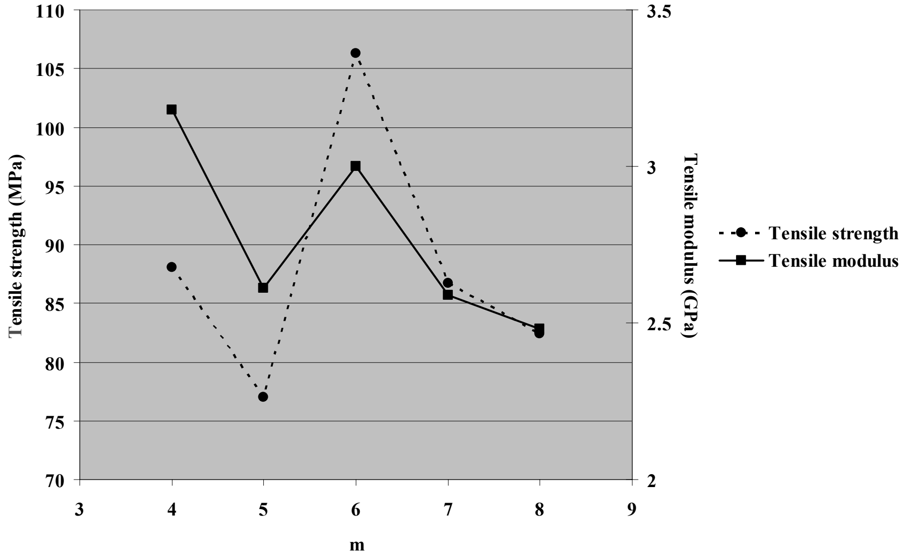


**Figure 5.** Polyamide tensile strength and tensile modulus vs. methylene spacer length (m)

**Table 2.** Tensile properties of polyamides

| Diamine | m | [ η ] (dL/g)[1] | $\sigma_b$ (MPa)[2] | E (GPa)[2] | ε (%)[2,3] |
|---|---|---|---|---|---|
| 1 | 4 | 1.04 | 88.1 ± 6.7 | 3.18 ± 0.18 | 3.4 ± 0.8 |
| 1 | 5 | 0.66 | 77.0 ± 2.4 | 2.61 ± 0.17 | 4.1 ± 0.4 |
| 1 | 6 | 0.77 | 106.3 ± 2.9 | 3.00 ± 0.03 | 6.3 ± 0.7 |
| 1 | 7 | 0.77 | 86.7 ± 0.8 | 2.59 ± 0.05 | 5.7 ± 0.6 |
| 2 | 7 | 0.89 | 76.0 ± 3.0 | 2.18 ± 0.07 | 5.6 ± 0.7 |
| 1 | 8 | 1.04 | 82.4 ± 2.5 | 2.48 ± 0.13 | 6.1 ± 0.5 |

1 Intrinsic viscosity determined in N-methyl-2-pyrrolidinone at 25.0 ± 0.1 ºC

2 Mechanical properties determined on thin films according to ASTM D662 at an extension rate of 0.51 cm/min (0.2 in/min)

3 Elongation at yield

## Conclusions

Polyamides derived from 3,6-bis(2-cyano-4-phenoxy)phthalonitrile were synthesized and shown to display odd-even dependence upon methylene spacer length with regards to the tensile properties (up to m=8). The polymers from even-numbered diacid chlorides had higher tensile properties and glass transition temperatures compared to the odd-numbered analogs. Polymer thermal stability appears to be independent of atmosphere during initial decomposition. The dielectric and electromechanical properties are currently under investigation to determine the effect of odd and even methylene spacer lengths and increasing methylene spacer length on the dielectric and electromechanical properties.

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## References

1. Kawai HJ (1969) Appl. Phys. 8:975
2. Scheinbeim JI, Newman BA (1995) Macromol. Symp. 98:897
3. Scheinbeim JI, Mei BZ, Newman BA (1995) Ferroelectrics 171:177
4. Murata Y, Tsunashima K, Koizumi N, Ogami K, Hosokawa F, Yokoyama K (1993) Jpn. J. Appl. Phys. 32:L849
5. Umemura J, Murata Y, Tsunashima K, Koizumi N (1999) J. Polym. Sci. Part B: Polym. Phys. 37:531
6. Fukada E (1998) Jpn. J. Appl. Phys. 37:2775
7. Zhang QM, Bharti V, Zhao X (1998) Science 280:2101
8. Wang X, Takahashi Y, Iijima M, Fukada E (1995) Jpn. J. Appl. Phys. 34:1585
9. Tajitsu Y, Ohigashi H, Hirooka A, Yamagishi A, Date M, Hattori T, Fukada E (1996) Jpn. J. Appl. Phys. 35:5199
10. Seo I (1995) Ferroelectrics 171(1-4):45
11. East A, Conciatori A US Patent 5,061, 760, 1991
12. Klein DJ, Bryant RG J. Polym. Sci. Part A: Polym. Chem. in press