Dielectric Properties of Poly(enaminonitrile)s

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(Received June 9, 1999)

ABSTRACT: Poly(enaminonitrile)s (PEANs), a new class of thermally stable aromatic polymers, possess excellent thermal stability, good mechanical properties and are easily soluble in many organic solvents. Flexible, tough films can be cast from these solutions. These polymers undergo a 'curing' reaction at 300–350°C to insoluble, more dimensionally stable materials without evolution of volatile byproducts. We summarize here the dielectric data measured at a frequency of 100 kHz, 25°C for some PEANs, and discuss the results in relation to their structures.

KEY WORDS Poly(enaminonitrile) / Dielectric Constant / Thermally Stable Polymer / Structure-Property /

The production of thermally stable organic polymers has been the subject of many research efforts for the past 30 years because of the growing application of thermally stable polymers in the fields of aerospace and electronics.^{1,2} Most of thermally stable polymers synthesized are aromatic, rigid-rod type polymers that have difficulties in processing due to their low solubility and high glass transition or melting temperatures. Therefore, compromises have been necessary between thermal stability and processability. A common approach has been to synthesize a flexible polymeric precursor which upon subsequent treatment, curing, cyclizes intramolecularly to produce the final thermally stable polymers. Polyimides are a familiar and successfully applied example of this approach and one of the fastest growing materials among polymers for electronic applications.

Even though polyimides meet most of the required properties in current microelectronic applications some disadvantages such as instability of the poly(amic acid) precursor and the emission of a small molecule byproduct (usually water or methanol) in the curing process is evident.

Poly(enaminonitrile)s (PEANs), are soluble, high molecular weight polymers which can be cured thermally without evolution of volatile byproducts. These polymers are stable hydrolytically before curing and exhibit excellent thermal stability and good film-forming properties. The dielectric constant, however, was found to be rather high initially (*ca.* 6) presumably because of the strongly polarized enaminonitrile linkage in the polymer backbone. A cured sample of a typical structure had a dielectric constant of around 5.³

The dielectric behavior of a polymer is determined by the charge distribution in the macromolecule which depends on a number of factors, including polarity of the bonds, molecular configuration, and morphology.

Microscopically the dielectric constant of a material

reflects the alignment of dipoles and the net polarization of the molecules which is attributed to restricted movement of charges within the material. In an electric field, positive charges move with the electric field and an equal number of negative charges move against it resulting in no net charge anywhere in the sample. However, there is a net positive charge at the surface toward the negative side of the field and a negative charge at the surface of the positive side. This process is called polarization. There are three basic components of this polarization, *i.e.*, electronic, atomic, and orientation polarization. Both electronic and atomic polarizations are caused by the displacement of positive and negative charge centers within the molecule. If the polymer molecule already possess a permanent dipole moment it will tend to be aligned by the applied electric field to give a net polarization in that direction. This is the most important type of polarization for the polymers containing very polar groups discussed in this work.

Clausius and Mossotti derived an equation which can be used to relate polarizability to dielectric constant of nonpolar or weakly polar polymers⁵ and Kirkwood developed an equation for polar liquid which can be used as a rough approximation for a polar polymer.^{4,6}

According to the equation, the dielectric constant of a polymer depends on the number of polar groups per unit volume, the square of the permanent dipole moment and the reciprocal of the absolute temperature. Therefore, by incorporating fewer polar groups per unit volume of a polymer is expected to result in a material with a lower dielectric constant.

To control the dielectric constant of PEANs, a series of PEANs having various aromatic moiety in the bis(chlorodicyanovinyl) aromatic monomers were synthesized with aromatic diamine comonomers. Rigid, rod-like aromatic residues such as naphthalene, biphenyl and terphenyl were employed. These groups might decrease dielectric constant of PENAs by increasing

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chain rigidity and diluting the polar enaminonitrile group per unit volume. PEANs with diamines containing less polarizable linking groups than O atoms like isopropylidene were also prepared. Further study on the dielectric properties of PEANs upon curing is in progress, however, it is out of scope of this paper.

EXPERIMENTAL

Monomers

1,4- and 1,3-Bis(chlorodicyanovinyl)benzene and 2,6-bis(chlorodicyanovinyl)naphthalene monomers were synthesized using the modified procedure previously reported.^{3,7} Monomers containing biphenyl and terphenyl moieties were also synthesized by the procedure developed in our group.⁸ All the diamines used for this study were purified by standard procedures.

Polymer Synthesis

Equimolar quantities of the appropriate monomers and diamines were mixed, under nitrogen, at room temperature in dry *N*-methyl pyrrolidone (NMP). LiCl was used in some polymerization systems to improve polymer solubility. To this reaction mixture, two equivalents of [2.2.2]diazabicyclooctane (DABCO) were added as an acid acceptor. The resulting viscous yellow mixture was heated under nitrogen for 24 h at 70–80°C and poured into vigorously stirred water. The precipitated polymer was dissolved in *N,N*-dimethylformamide (DMF) and reprecipitated into methanol/water. The polymers were dried at 120°C *in vacuo* (0.1 Torr) for 72 h.

Characterization

All the polymers were characterized by IR, ¹H NMR, and ¹³C NMR. Viscosities of the polymer solutions were measured in an Ubbelohde viscometer. Thermal analysis (DSC and TGA) of the polymers was carried out on a Perkin-Elmer 7 Series Thermal Analysis System. The glass transition temperature was taken as the mid point of the heat capacity change in DSC. The capacitance of structures composed of thin films upon which metal electrodes had been sputtered was measured with a precision bridge (HP 4274LCR meter). The dielectric constants were obtained by dividing the capacitance by the electrode area.

RESULTS AND DISCUSSION

A series of PEANs with various structure were prepared as the polymerization scheme shown below. These polymers possess moderate to high molecular weight judging from the intrinsic viscosity and formed flexible films. The glass transition temperatures determined by DSC ranged from 200 to 300°C depending on the structure. As expected, flexible links such as ether and isopropylidene group lower the *T_g*, while biphenyl and terphenyl moieties increase the *T_g*.

The thermal stability of PEANs was measured by TGA and some of the results are included in Table I. All the polymers exhibited good to excellent thermal stability in both air and nitrogen. Most of the polymers decomposed completely in air above 600°C but retain 70–80% of

Table I. Characteristics of PEANs

No.	Polymer	$[\eta]_{\text{DMF}}^{25^\circ\text{C}}$	10 wt% loss in $\text{N}_2/^\circ\text{C}$	T_g °C
1	Ib	0.72	566	274
2	IIIb	0.59	574	280
3	IVb	0.38	600	
4	Vb	0.42	640	
5	Ic	0.51	509	255
6	IIc	0.51	506	228
7	IVc	0.43	520	
8	IIa	0.55	578	278
9	If	0.41	618	250
10	IVe	0.30	610	
11	Id	0.44	487	208
12	Ig	0.35	470

Scheme 1.

initial weight at 1000°C in nitrogen. Even though the direct comparisons of thermal stability between different structures are difficult because of the differences in the molecular weight and the presence of differing amount of low molecular weight oligomers, the general structural effects on the thermal stability in this series of polymers are clearly reflected. As the 10 wt% loss-temperatures show in Table I, flexible links such as ether and isopropylidene groups have a detrimental effect on thermal stability. Aromatic or rigid groups enhance the thermal stability with marginal sacrifice in their solubilities.

Previous work³ showed that PEANs could be cyclized without evolution of volatile by-products to a cured insoluble polymer containing substituted quinoline structures. DSC analysis showed broad exothermic transitions with the peak maximum at around 350°C for all the polymers. When the samples were cooled and rescanned, no exotherms were observed. TGA did not show any weight loss in this temperature range indicating

the occurrence of a thermally induced cyclization or curing reaction without generating volatile by-products.

The dielectric behavior of a polymer is determined by the charge distribution in the macromolecules. The charge distribution in a polymer depends on a number of factors, including polarity of the bonds, molecular configuration, and morphology. The enaminonitrile structure endows the polymer with good solubility in many organic solvents as well as imparting hydrolytic stability in contrast to the poly(amic acid) precursors to polyimides which are sensitive to hydrolysis. However, because of this highly polarized group on the backbone, the polymer showed relatively high dielectric constants (>5) as was reported earlier (for comparison, the dielectric constant of Kapton is approximately 3.6).³ The pronounced dipolar character of these materials is evident in the carbon NMR spectra of enaminonitriles. The differences in chemical shifts of the olefinic carbon atoms bearing the amino and nitrile groups (carbon 1 and 2 of the following structure) are around 110 ppm for all the polymers prepared in this study.

Dipole moments⁹ of the following two molecules, I and II, also illustrate this fact.

I

$$\mu_{\text{cal}} = 3.41 \text{ D}$$

$$\mu_{\text{exp}} = 3.37 \text{ D}$$

II

$$\mu_{\text{cal}} = 5.40 \text{ D}$$

One of possible approaches to reduce this apparent high dielectric constant could be the introduction of rigid and more aromatic moieties in the chain and/or less polar linking group between the aromatic backbone.

The dielectric constants of several of the new polymers were measured and are shown in Table II. The constants ranged from 3.6 to 5.2 depending on the structure. For easy comparison, samples 1 to 4 represent polymers from four different bis(chlorodicyano) aromatic monomers (1,4-phenyl, 2,6-naphthalene, biphenyl, and terphenyl monomer, respectively) and the same oxydianiline comonomer. Samples 5 to 7 represent polymers from the aromatic monomers (1,4-phenyl, 1,3-phenyl, and 4,4'-biphenyl) and 1,4-bis(*p*-aminophenoxy) benzene comonomer. Samples 8 to 12 are other polymers from different pair of monomers. As shown in the Table II, an overall decreasing tendency in the dielectric constant values of more rigid and aromatic ring structures can be observed. The decrease of the dielectric constant was effected by diluting the polar enaminonitrile group within the same repeating unit and also by decreasing the flexibility of the polymer chains. Less polar linking group such as isopropylidene group will also give the same result by

Table II. Dielectric constant of PEANs at 100 kHz, 25°C

No.	Polymer	ϵ	Molar volume
			cm ³ mol ⁻¹
1	Ib	(6.00)	327.3
2	IIIb	4.69	373.8
3	IVb	4.95	392.8
4	Vb	4.30	458.3
5	Ic	4.21	400.8
6	IIc	4.08	404.3
7	IVc	3.94	466.3
8	IIa	5.27	257.3
9	If	4.91	346.3
10	IVe	4.53	384.8
11	Id	3.67	486.3
12	Ig	4.04	419.0

the 'dipole dilution effect' which should give lowered dielectric constants. Polymer samples 5 to 7 from 1,4-bis(aminophenoxy)benzene comonomer show lowered values compared to those of corresponding polymers from oxydianiline comonomer because of the additional phenoxy group in their repeating units which occupies volume without contributing significantly to the net dipole moment of the molecules. Polymer sample 11, from 1,4-bis(chlorodicyanovinyl)benzene monomer and Bis-M diamine (diamine d in Scheme 1) showed the lowest value (3.67) among the samples, which might be attributed to the non-polar, and rather bulky isopropylidene groups in the repeating unit. This low value is compared to that of sample 5 (4.21) which contains slightly polar ether linkage in the analogous backbone structure. Sample 8, from 1,3-bis(chlorodicyanovinyl)-benzene monomer and 1,4-phenylene diamine showed the highest value (5.27), where polar enaminonitrile groups are more concentrated within a given volume.

Dielectric constant of polymer 10 (4.53) and 2 are lower than that of polymer 3 (4.95) which has a larger repeating unit volume. This discrepancy may be the result of the absence of the ether linkage of polymer 10, resulting in a more rigid structure which makes orientation of the polar groups more difficult. The oxygen atom should also affect the net dipole moment. Polymer 2 has naphthalene ring which is more rigid than the biphenyl group. Polymer 12 and 7 have small difference in dielectric constants compared to the difference in repeating unit volumes. This result could be caused by the bulky group which occupies volume without contributing significantly to the net dipole moment of the molecules. The steric constraint may also prevent the large dicyano groups from being located on the same side of the molecules, resulting in a reduction of the net dipole moment.

Orientation polarization is a relatively slow process compared with electronic and atomic polarization.⁴ 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.¹⁰ When the polar molecules are very large or the viscosity of the medium is very high, the rotating motions

Table III. Dielectric constants of poly(enaminonitrile)s **3**, **7**, and **10** before and after soaking in water

Frequency kHz	ϵ (before being soaked)			ϵ (after being soaked)		
	3	7	10	3	7	10
0.1	5.19	4.08	4.77	5.88	4.53	6.03
0.2	5.16	4.07	4.74	5.84	4.51	5.94
0.4	5.14	4.06	4.72	5.81	4.50	5.87
1	5.10	4.04	4.68	5.77	4.47	5.78
2	5.08	4.03	4.66	5.75	4.46	5.73
4	5.06	4.02	4.64	5.72	4.44	5.69
10	5.04	4.00	4.61	5.69	4.42	5.63
20	5.01	3.99	4.59	5.66	4.41	5.59
40	4.99	3.97	4.57	5.64	4.39	5.55
100	4.95	3.94	4.53	5.60	4.36	5.50

Table IV. Water absorption and dielectric constant change of poly(enaminonitrile)s

Polymer	Water absorption	Dielectric constant change at 100 kHz
	%	%
3	3.17	13.3
7	2.41	11.0
10	2.24	26.4

of the molecules are not enough to reach equilibrium with the field. The polarization then requires 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 usually dissipation of thermal energy. The complex dielectric constant of the dielectric material is expressed as $\epsilon^* = \epsilon' - i\epsilon''$ where ϵ' is the measured dielectric constant of the dielectric material in the condenser and ϵ'' is the imaginary part of the dielectric constant, commonly known as the loss factor. The ratio ϵ''/ϵ' is $\tan \delta$ or tangent of the dielectric loss angle, which is usually called the dielectric loss tangent or the dissipation factor.

$$\tan \delta = \epsilon''/\epsilon'$$

Normally, dielectric constant and high-frequency dielectric loss are characteristics of the chemical structure of the polymer. At low frequencies, the dielectric loss becomes increasingly sensitive to small amounts of moisture and other impurities. If there is a significant amount of residual solvent or ionic impurity in the sample, $\tan \delta$ would be high at low frequencies and much lower at higher frequencies.

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

Figure 1. Plot of dissipation factor ($\tan \delta$) vs. frequency for PEAN **3** before and after being soaked in boiling water for 3 h, and after being redried in vacuum at 110°C for 3 days. **Figure 2.** Plot of dissipation factor ($\tan \delta$) vs. frequency for PEAN **10** before and after being soaked in boiling water for 3 h, and after being redried in vacuum at 110°C for 3 days.

constant returned to their initial values, *i.e.*, 5.10 at 100 Hz, 25°C for polymer **3**. As shown in Figures 1 and 2, the $\tan \delta$ for polymers **3** and **10** changes very little over the frequency range examined, indicating that the polymer samples were free of any significant amount of impurities. After the film was soaked in water, the $\tan \delta$ of polymer **10** showed the characteristic changes caused by absorbed water. In Figure 2, $\tan \delta$ rapidly decreased as frequency increased. However, polymer **3** and **7** did not show such behavior over the frequency range studied. It seems that a frequency lower than 100 Hz should be used to observe absorbed water effect on $\tan \delta$. These results support the contention that the relatively high dielectric constants of polyenaminonitriles is a direct result of their highly polarized structure and is not caused by molecules absorbed in the films.

Because the main structural factor contributing to the

Figure 3. Plot of dielectric constant vs. molar volume of repeat unit.

net polarizability of the molecule seems to be the high polarity of the enaminonitrile linking group in this polymer, it was of interest to correlate the observed dielectric constants with the molar volume values of the repeating unit of each polymer. Figure 3 shows a plot of dielectric constant vs. molar volume of the different polymer. The molar volumes were calculated from the group contribution parameters of Van Krevelen.¹¹ As the molar volume increases, a decrease in the dielectric constant was seen, with some deviations. These results clearly show the 'dipole dilution effect' on the dielectric constant of polymer as was expected from the Kirkwood equation previously discussed.^{4,6} However, a quantitative explanation is difficult because of the complexity of the factors which determine the dielectric constant, such as chain rigidity and contributions of other less-polar groups, and even small amount of residual solvents in the polymer samples. Finally, It should be mentioned that we have to consider the trade-off relationship among the dielectric property, thermal stability, solubility

(processability) and other properties in the final selection of a good dielectric material.

In summary, a lower dielectric constant could be obtained by introducing more rigid aromatic rings and/or less-polar linking group in this polymer system. The introduction of hexafluoroisopropylidene units or aromatic ring with bulky pendant group in the polymer backbone seems to be a likely choice as the next design modification which should lower the dielectric constant without causing significant loss of thermal stability and solubility of these materials. Preliminary results from an examination of the effect of high temperature on the dielectric constant are too complicated to discuss at this time, because of the occurrence of the curing reaction, even at temperature significantly below 350°C.

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