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"Poly(enaminonitriles): Novel Materials for Use in Electronics"

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J. A. Moore, Douglas R. Robello and Parag G. Mehta

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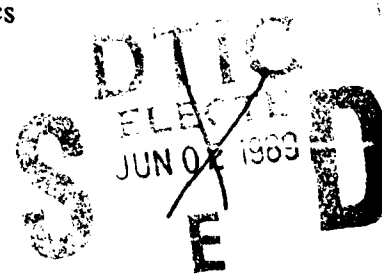Poly(enaminonitriles): Novel Materials for Use in Electronics

by

J. A. Moore[*], Douglas R. Robello[1] and Parag G. Mehta
Department of Chemistry
Polymer Science and Engineering Program
Rensselaer Polytechnic Institute
Troy, NY 12180-3590

ABSTRACT

Three new bis(1-chloro-2,2-dicyanovinyl) benzene monomers have been synthesized. Polymerization of these monomers with two different diamines led to moderate to high molecular weight polyenaminonitriles possessing excellent thermal stability. These polymers cure without emission of volatile byproducts. Initial thermal, mechanical and dielectric data of these polymers is presented. The dielectric constant of a representative polymer was found to be approximately 8 before heat treatment and 5 afterward.

1. INTRODUCTION

The growing need for novel polymer possessing excellent thermal stability by the electronics and aerospace industries has provided researchers with the impetus that led to the discovery of a variety of polymeric materials[2]. The structural requirements for such polymers include incorporation of chemical bonds of high dissociation energy, the presence of functional groups in the polymer backbone that crosslink upon heating and inflexible chains. Aromatic moieties in a molecule normally endow the polymers with superior thermal stability. Because the most common mechanism for the degradation of the polymers is oxidative in nature, incorporation of heterocyclic units further improves thermal stability by increasing char yield at very high temperatures. Polymers possessing these structural features generally are difficult to process because of their low solubilities and high glass transition or melting temperatures. These conflicting trends often lead to a processability-thermal stability tradeoff.

A common approach to solve the problem of processability is to synthesize a more flexible prepolymer which upon subsequent treatment ("curing") cyclizes intramolecularly to produce the final thermally stable, rigid rod polymers. Polyimides[3] are a familiar and successfully applied example of this approach. The principal drawback to the curing reaction of polyimide and other similar polymers is the emission of volatile molecules which are

trapped in the bulk of high molecular weight polymer. The difficulties in removing these small molecules from the bulk polymer without causing voids has restricted the use of many polyimides to various thin-film applications. Besides this result, the intermediate polyamic acid (prepolymer) suffers from poor hydrolytic stability. We, therefore, reasoned that the presence of suitable functional groups in a prepolymer which can undergo intramolecular cyclization by structural rearrangement will yield cured polymer *without the emission of volatile byproducts*. Recent work[4] from our laboratory has demonstrated the successful application of this approach to the preparation of several new polymers employing vinylic nucleophilic substitution reactions.

2. EXPERIMENTAL

2.1 Monomer Synthesis

Bis (1-chloro-2,2- dicyanovinyl)benzene monomers[4] were readily synthesized from the corresponding diacid chlorides as shown in Scheme I.
1,3-Bis(4-aminophenoxy-4'-benzoyl)benzene was prepared according to a literature procedure[5] and was purified by two recrystallizations from 1-butanol.
4-Aminophenylether (Gold label quality) was obtained from the Aldrich Chemical Company and was used as received.

2.2 Polymer Synthesis

Method A: Equimolar quantities of the appropriate bis(1-chloro-2,2-dicyanovinyl) benzene monomer and 4-aminophenylether were mixed, under nitrogen, at 23 °C in dry N-methyl pyrrolidone (NMP) in the presence of two equivalents of 4-(dimethylamino)pyridine (DMAP) as an acid acceptor. The reaction mixture turned brown and then yellow. The mixture was heated under nitrogen for 18 hours at 70 °C, cooled to room temperature and poured into vigorously stirred water. The precipitated polymer was dissolved in N,N-dimethylformamide (DMF) and reprecipitated into methanol.

Method B: Equimolar quantities of a particular bis(1-chloro-2,2-dicyanovinyl) benzene monomer and 1,3-bis(4-amino phenoxy- 4'-benzoyl)benzene were mixed, under an argon atmosphere, at 0°C in dry NMP in the presence of one equivalent of 1,4-diazabicyclo [2.2.2] octane (DABCO) (purified by sublimation prior to use) as acid acceptor. The mixture immediately turned brown and then yellow (ca. 1 minute). The mixture was allowed to warm to room temperature over 1 hour and then heated at 70-75 °C for 24 hours. The viscous solution was cooled and poured into vigorously stirred water and the precipitated polymer was filtered. The polymer was further purified by one more precipitation from NMP into water followed by extraction with methanol in a Soxhlet apparatus for 24 hours. The polymers were dried at 130-135 °C *in vacuo* for 24 hours.

2.3 Characterization

All six polymers were characterized by IR, ^{1}H NMR and ^{13}C NMR. Viscosities of the polymer solutions were measured in an Ubbelohde viscometer. Thermal analysis (DSC, TGA and TMA) of the polymers was carried out on a Perkin-Elmer 7 Series Thermal Analysis System. Dynamic mechanical analysis was performed using a Rheovibron instrument. Dielectric constant of polymer F was measured with a GenRad 1689 Precision RLC Digibridge. Sample thickness was measured with a Danatron digital electrogauge. Aluminum electrodes

(2000 A°) were applied on both sides of the polymer film by vacuum deposition. The dielectric constant, ε, was calculated as follows.

$$\varepsilon = \frac{(Capacitance \ in \ pF)(Thickness \ in \ \mu m)}{(area \ in \ cm^2)(885.4)}$$

3. RESULTS AND DISCUSSION

3.1 Synthesis

There are primarily two reasons for the choice of bis(1-chloro-2,2- dicyanovinyl) benzene monomers.

1. The dicyanomethylidene group ($=C(CN)_2$) and the carbonyl group have similar inductive and resonance effects[6]. Thus the presence of dicyanomethylidene units imparts sufficient electrophilic character to the vinylchloride functionality to make it reactive toward nitrogen-containing nucleophiles.

2. The presence of suitably disposed nitrile groups further ensures that an enaminonitrile moiety, the initial product of a vinylic nucleophilic substitution reaction, can cyclize to a stable heteroaromatic aminoquinoline structural unit[3a]. (Scheme III)

An additional advantage of the enaminonitrile structural unit is that it endows the polymer with good thermal and hydrolytic stability (as opposed to the hydrolytic sensitivity of polyamic acids in the synthesis of polyimides) as well as making the polymer soluble in volatile, non-aqueous solvents.

Hergenrother's success in using 1,3-bis-(4-aminophenoxy-4'-benzoyl)benzene as a monomer which confers both toughness and solvent resistance on a series of polyimides which he studied[5] prompted us to try this compound in our system.

The polymers appeared to possess moderate to high molecular weight, judging from intrinsic viscosity measurements (Table 1) and the fact that fingernail-creasable films could be cast from their solutions in DMF and NMP.

3.2 Thermal and Mechanical Properties

As shown in Table 1, all polymers possess good to excellent stability in both air and nitrogen (see also Fig. 1 and 2). The polymers decompose completely in air above 550 °C but retain approximately 70 % of their mass at 900 °C in nitrogen. Differential scanning calorimetry (DSC) of all six polymers showed a somewhat broad exotherm, starting near 300 °C and reaching maximum intensity near 350 °C. This peak was completely absent when the samples were cooled and rescanned (Fig. 3). This phenomenon is believed to indicate the occurence of a thermally induced cyclization reaction as shown in Scheme III for polymer F.

Polymers F, G and H did not show any prominent glass transition in DSC while polymers I, J and K showed distinct glass transition temperatures (Fig. 3). This result may be caused by the incorporation of unsymmetrical diamine E, especially the central benzene ring with 1,3- entrainment, which may have resulted in a substantial decrease in the ordered arrangement of polymer chains.

To understand further the structure-property relationship and to assess their usefulness for advanced applications, it is necessary to analyze these polymers under various stress-strain conditions. Furthermore, the knowledge of dynamic moduli and other related properties can also pave the way for the design of novel

polymers having better properties. Polymer F was chosen for preliminary study and initial data is shown in Fig. 5 which contains the plots of E' (storage modulus) and E" (loss modulus) versus temperature for uncured and cured polymer and Kapton. The glass transition for the uncured polymer occurs around 270-280 °C as indicated by the decrease in the value of E'. Cured polymer, as expected, does not show any glass transition when heated to 384 °C. In the glassy state (below the glass transition temperature) molecular motions are largely restricted to vibrations and short range rotational motions and hence E' does not change appreciably over a wide temperature range. Because polymer F starts undergoing a curing reaction at ~300 °C, measurements of E' beyond this range are not meaningful. Under the same experimental conditions, Kapton appears to undergo a glass transition at approximately 304 °C.

The transitions evident in the loss modulus curve are reminiscent of those which have been attributed to motion about the chain backbone or to the motion of side chains[9]. These phenomena could be an outcome of at least two processes which we are studying via dynamic NMR techniques[7]:

1. Rotation around the double bond of the vinylidene cyanide group.

2. Rotation about the vinyl carbon-nitrogen single bond in enaminonitrile moieties.

Polymer F was further investigated by thermomechanical analysis (TMA). As shown in Fig. 6, the extent of penetration was measured as a function of temperature for both cured and uncured polymers. For an uncured polymer, the glass transition temperature was detected around 260-270 °C in accord with the dynamic mechanical analysis discussed above. It can be readily seen that such a transition is absent in the case of the cured polymer. An Instron test of this polymer gave the following results.

Polymer	Average Breaking Stress	Average Breaking Strain
Uncured	136,000 psi	4.2 %
Cured	131,000 psi	2.9 %

Cured polymer seems to be slightly more brittle and less elastic as indicated by the lower values of average breaking stress and strain. It should be noted that these samples have not been optimized with respect to molecular weight or distribution. A detailed analysis of the mechanical data will be presented in a future publication.

3.4 Dielectric Behavior

Upon interaction with an electric field the charges within the polymer experience restricted movement giving rise to a net dipole moment which, in turn, determines the dielectric constant of the material. Thus, the dielectric property of a polymer is determined by the charge distribution in the macromolecule. The charge distribution in a polymer depends on a number of factors[8]:

1. Polarity of the bonds between the atoms constituting a given structural unit. This structural feature translates into the net polarity of the structural units in the molecule. These dipolar structural units are easily affected by thermal motion.

2. Overall molecular configuration including symmetry in the molecule.

3. Morphology of a polymer.

In the case of polyenaminonitriles, there is a strong charge asymmetry in the vinylic double bond bearing two nitrile groups (acceptor) and a secondary amino group (donor). This polarization of the double

bond is clearly reflected in the ^{13}C NMR spectra of these polymers. Difference in the chemical shifts of the two carbon atoms of the double bond in question is approximately 110 ppm. High concentration of these dipolar enaminonitrile structural units (two per repeat unit) results in a dielectric constant as high as 8 for polymer F. As can be seen in the Table II, the dielectric constant shows very little frequency dependence. After heat-curing, the dielectric constant decreases to 5. This change in the dielectric constant can be explained qualitatively. Upon heat-curing, one of the nitrile groups is consumed. This occurrence, coupled with the fact that the double bond bearing a nitrile and an amino group now become part of the aromatic system thereby effectively participating in the electron delocalization in the quinoline ring system, results in a net decrease in charge asymmetry and also interferes with the efficiency of electron delocalization between the amino group and the nitrile group.

3.5 Curing

All six polymers were cured (Scheme III) by heating at approximately 400 °C in an inert atmosphere and the curing was monitored using IR spectroscopy. As shown in Fig. 4, for polymer F, the enamine N-H stretching band at 3260 cm^{-1} disappeared and was replaced by two new bands at 3365 and 3480 cm^{-1} which are characteristic of a primary aromatic amine. At the same time, the nitrile band near 2210 cm^{-1} decreased to approximately half its original intensity. The above data is consistent with a rearrangement, at least in part, of the enaminonitrile repeat unit into a 4-aminoquinoline unit[4a] (Scheme 3).

4. CONCLUSION

We have successfully employed dicyanovinylidenechloride monomers as synthetic equivalents of diacid chlorides to yield a new class of thermally stable materials possessing interesting properties.

Work to study the dielectric and dynamic mechanical properties of all the polymers further is underway.

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   Interscience: New York, 1986, Vol. 5,
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7. BIOGRAPHY

James A. Moore obtained a B.S. degre from St. John's University and a Ph.D degree from the Polytechnic Institute of Brooklyn in 1967. Thereafter he was a National Insitutes of Health Postdoctoral Fellow at the University of Mainz, West Germany, and a Research Associate at the University of Michigan in 1968. In 1969 he joined the faculty of the Chemistry Department of Rensselaer Polytechnic Institute where he is Full Professor of Organic and Polymer Chemistry. He is a member of the American Chemical Society, the Editorial Boards of Macromolecular Syntheses and Chemistry of Materials and is Associate Editor of Organic Preparations and Procedures International. Dr. Moore has more than 130 publications, including 6 books, and in 1985 was awarded the American Cyanamid Award for Significant Achievement in Synthesis.

Douglas R. Robello obtained a B.S. degree from Rensselaer Polytechnic Institute in 1978. After teaching High School Chemistry for three years, he joined Rensselaer Polytechnic Institute as a graduate student in 1982 and received his Ph.D degree in 1986. He is currently at Eastman Kodak Corporate Research Laboratory.

Parag G. Mehta obtained a B.Sc. degree from Gujarat University, Ahmedabad, India in 1982 and an M.Sc degree from Indian Institute of Technology, Bombay, India in 1984. Mr. Mehta is currently a graduate student at Rensselaer Polytechnic Institute where he expects to receive his Ph.D degree in September 1989. Mr. Mehta is a member of the American Chemical Society.
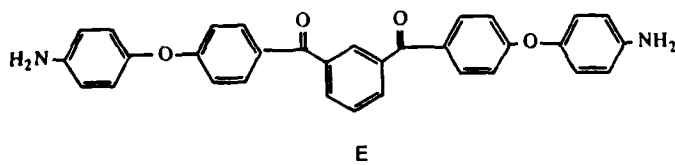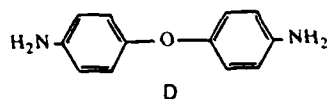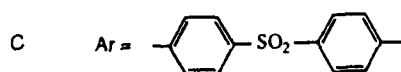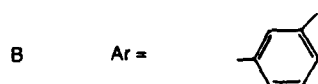
Scheme I

A   Ar =

B   Ar =

C   Ar =
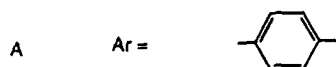
H_2N—〈 〉—O—〈 〉—NH_2

D

H_2N—〈 〉—O—〈 〉—NH_2

E
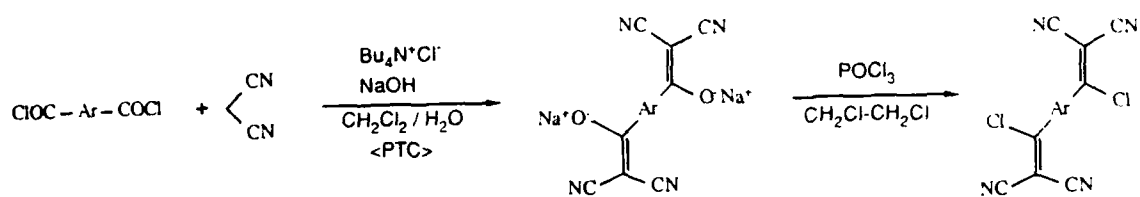
Fig. 1 TGA of polymer I in air and nitrogen atmosphere.
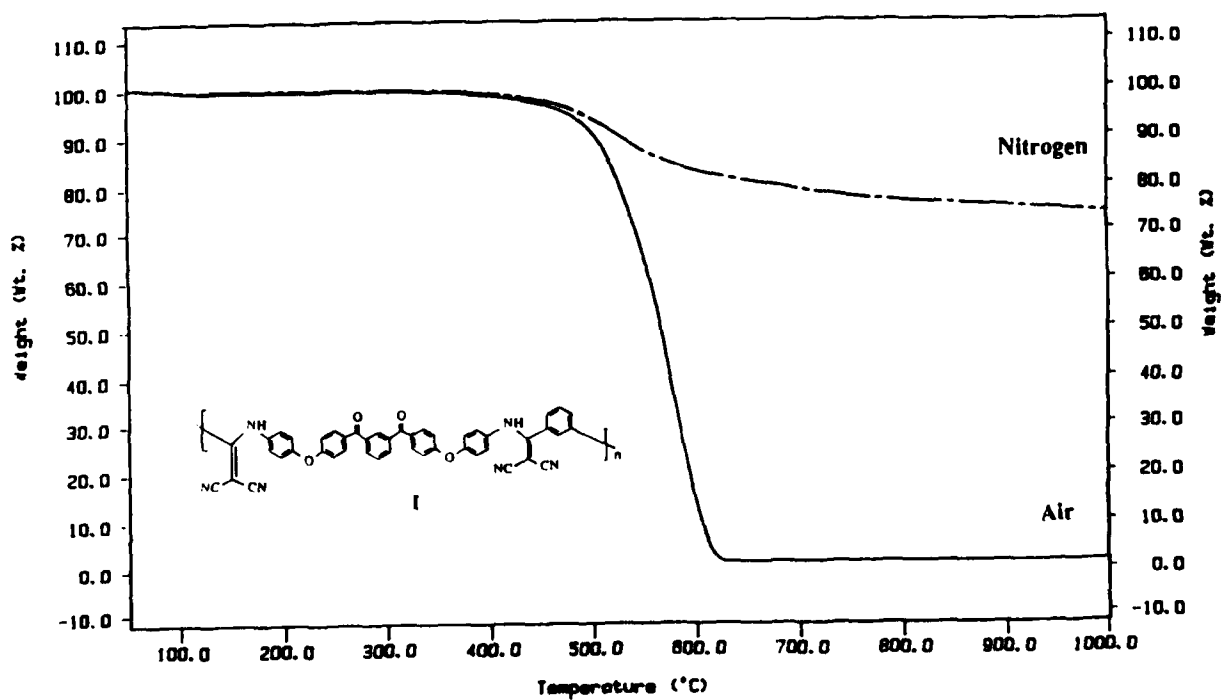
Scheme II
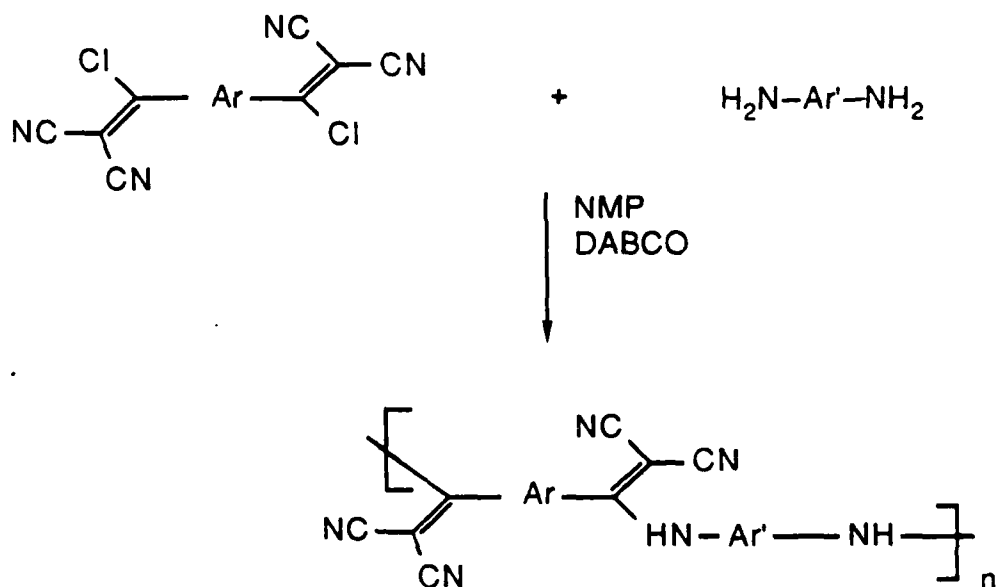
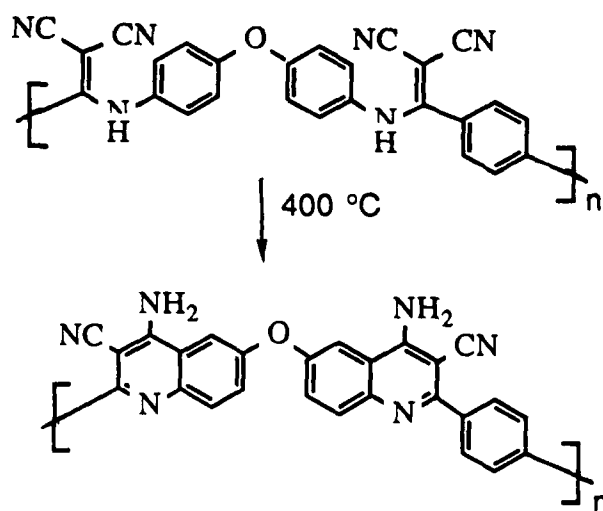| Polymer	Monomers	
F	A	D
G	B	D
H	C	D
I	A	E
J	B	E
K	C	E

Scheme III

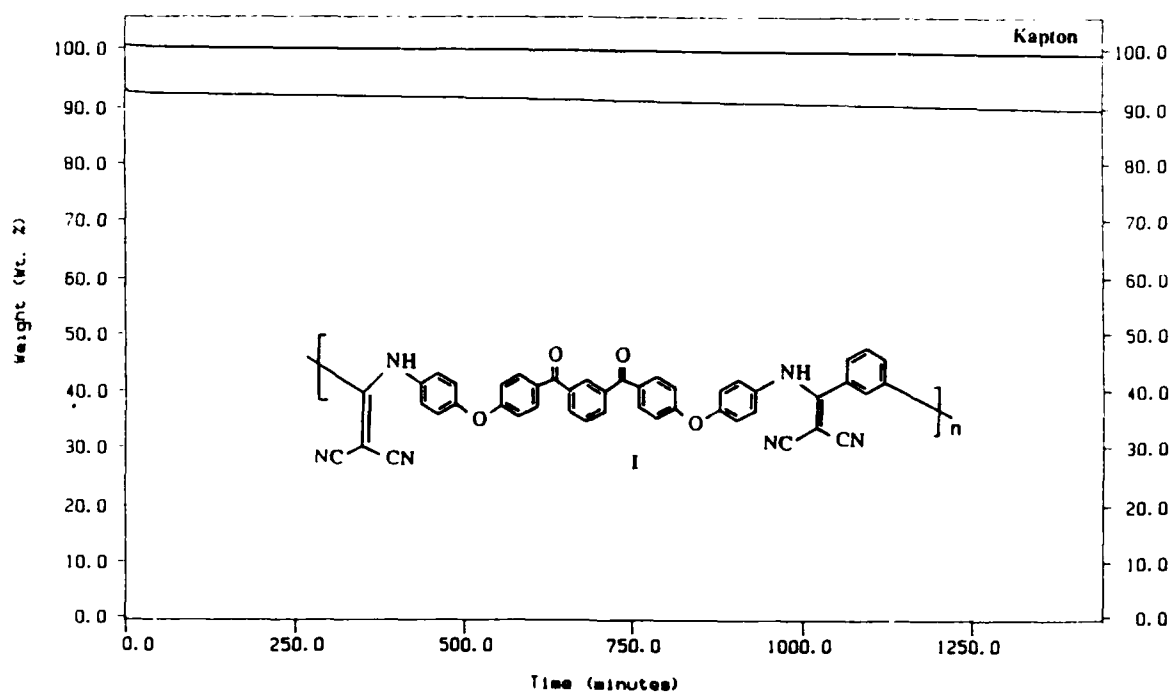Fig. 2 Isothermal aging of polymer I at 300 °C in air.

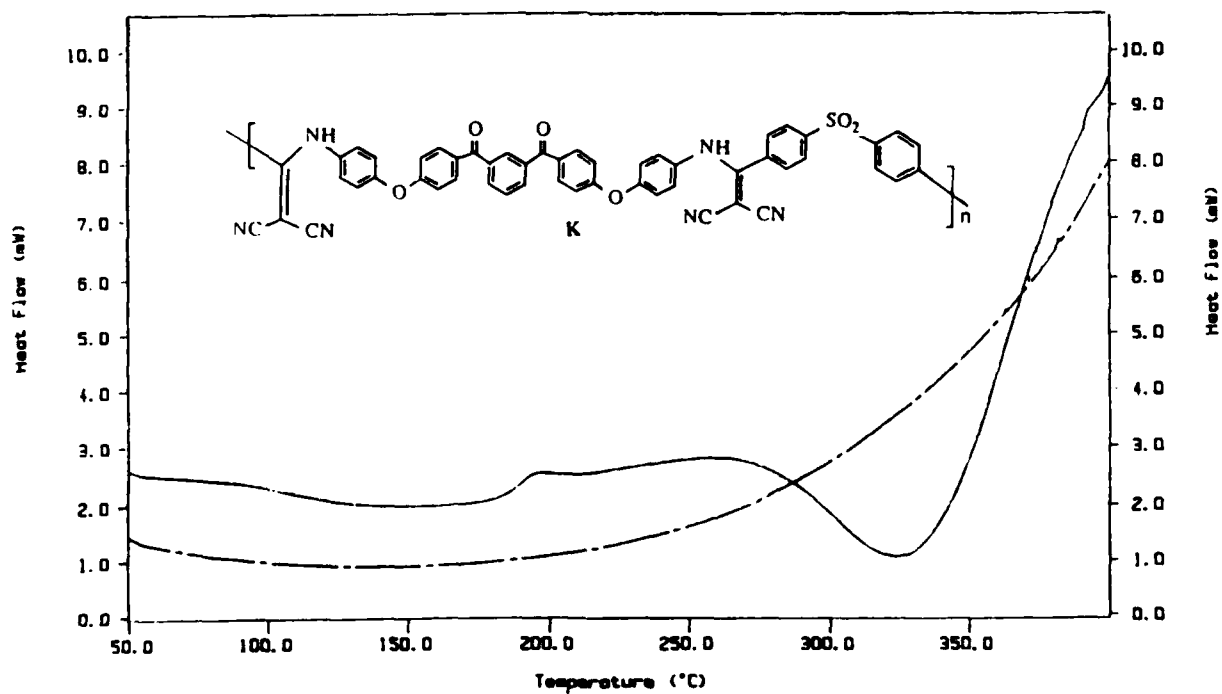Fig. 3 DSC of polymer K.

Fig. 4 IR spectra of Polymer F at 400 °C

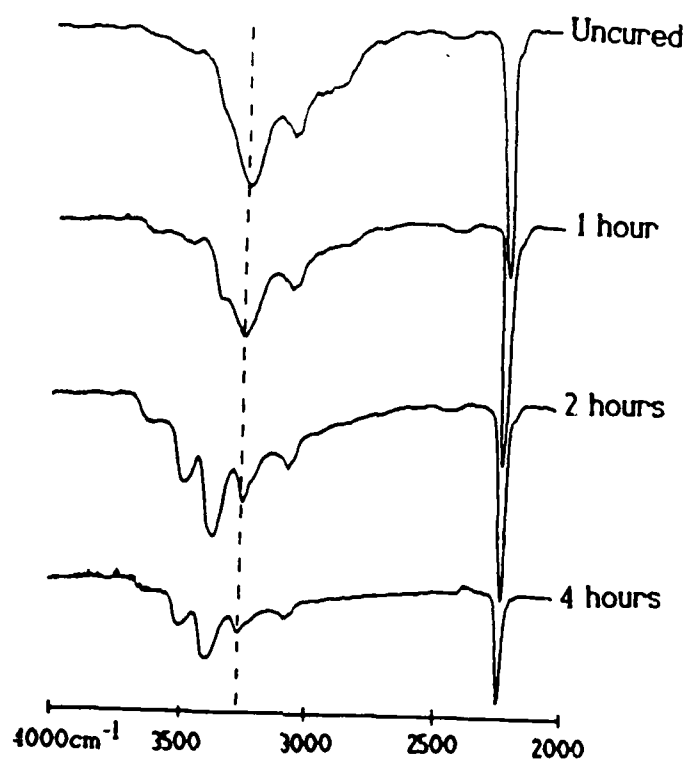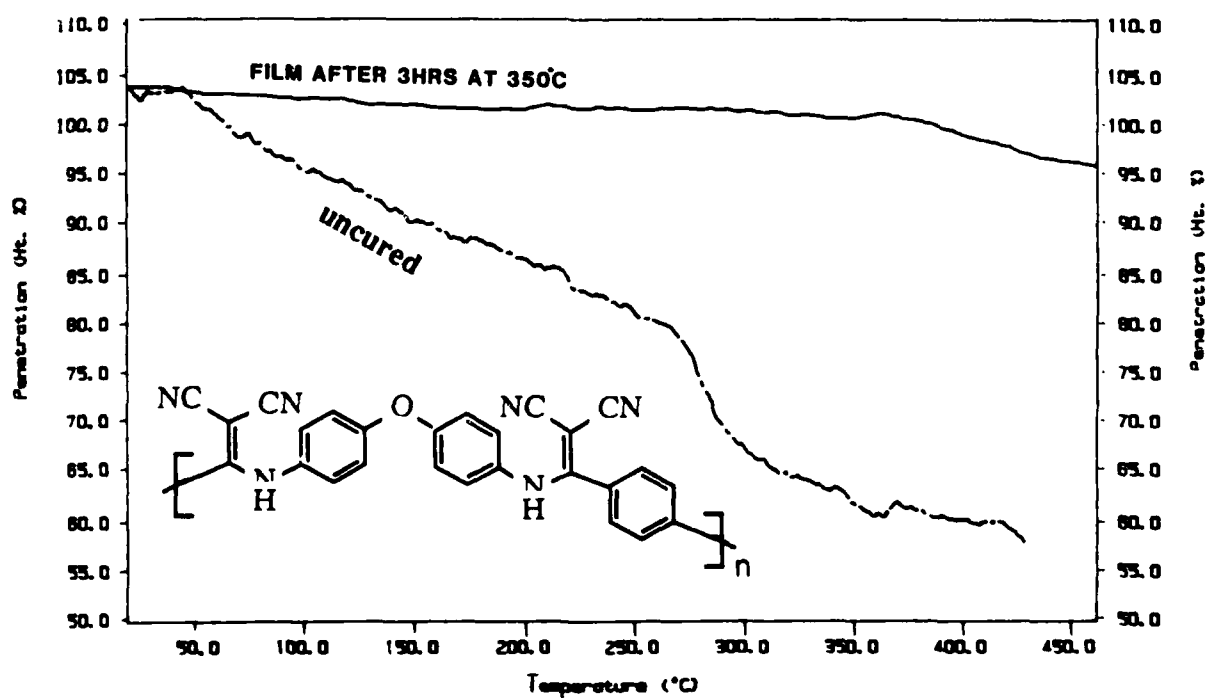## Fig. 6 Thermomechanical Analysis of polymer F.
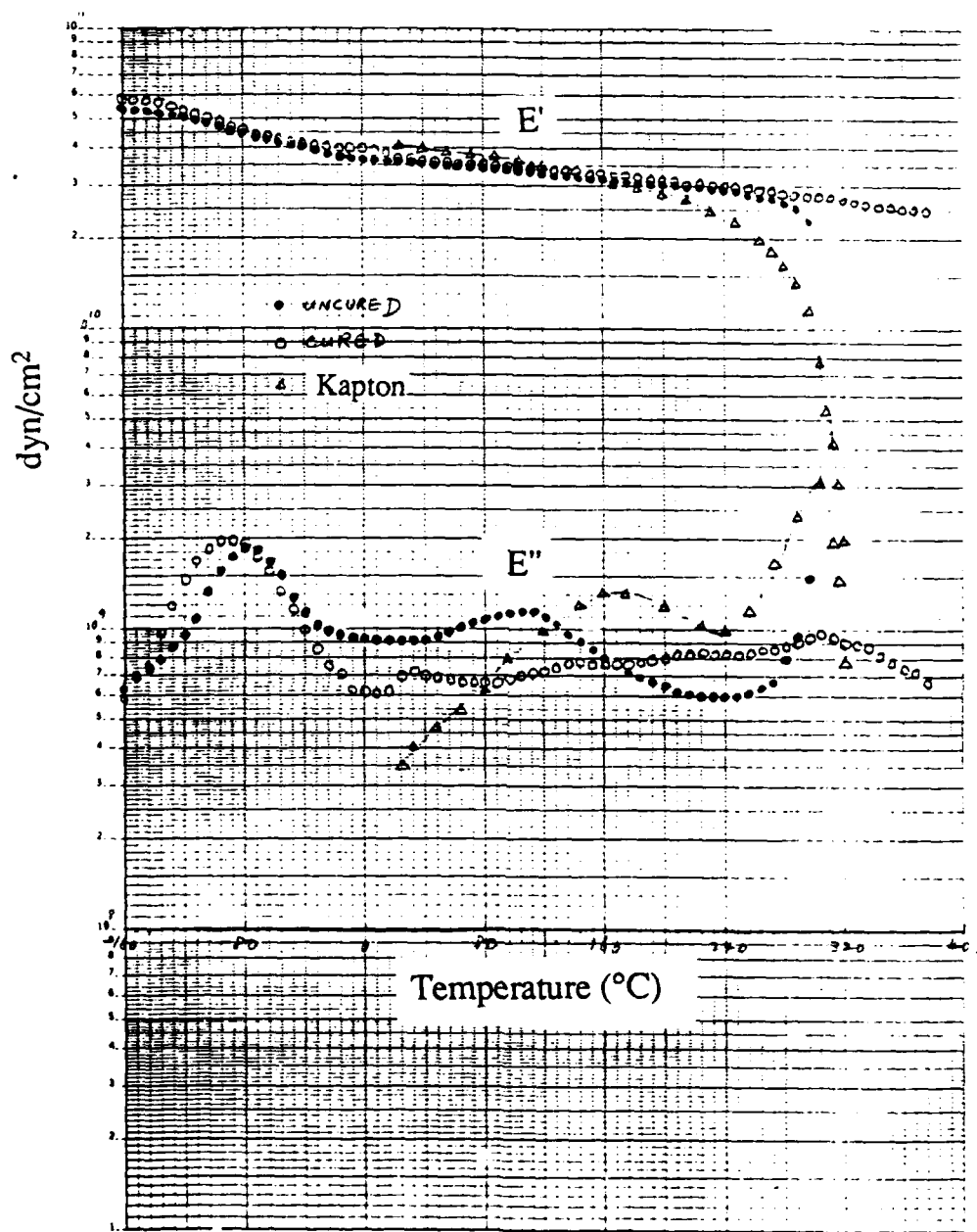
Fig. 5 Dynamic Mechanical Analysis of Polymer F

Table I: Characterization of Polymers

Polymer	$[\eta]$ (dL/g)	50% wt. loss temp.°C(air)	Residual wt. % 900 °C (N_2)	T_g (°C)
F	0.84[a]	505	73	260-270[d]
G	0.39[a]	477	71	-
H	0.68[a]	484	68	-
I	0.60[b]	569	73	164.3 (film)
J	1.99[b]	531	70	240.4 (powder)
K	1.83[c]	525	62	184.21 (powder) 237.35 (film)

a : In DMF at 25 °C
b : In DMAC at 25 °C

c : η_{inh} at conc. of 0.41g/dL in DMAC at 25 °C
d : Determined by TMA.

Table II
Dielectric Measurements for Films of Polymer F

test freq, Hz	capacitance, pF	ϵ	Dissipation Factor
Before Heat Curing[a]			
10^1	474.5	8.452	0.0437
10^3	456.9	8.146	0.0106
10^4	448.5	7.996	0.0089
10^5	446.9	7.968	0.0145
After Heat Curing[b]			
10^3	696.9	5.178	0.0042
10^4	689.9	5.126	0.0095
10^5	676.6	5.027	0.0368
10^6	658.7	4.894	0.2509

[a] Sample thickness 20.0 μm. Electrode area 1.27 cm^2; 24.0 °C.
[b] Sample thickness 7.5 μm. Electrode area 1.14 cm^2; 24.9 °C.