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13. ABSTRACT (Maximum 200 words) A program has been completed utilizing copolymerization and polymer blending methods to prepare polymer films with useful dielectric properties. A scaled-up procedure for the synthesis of 2-fluoroacrylonitrile and ethyl-2-fluoroacrylate has been developed. These monomers have been polymerized using free-radical methods and the polymer structures fully characterized. Both polymers are atactic. Films of poly(2-fluoroacrylonitrile) exhibit a dielectric constant at 8.9 while films of poly(ethyl-2-fluoroacrylate) have a dielectric constant of 4.0 (50 Hz). Blends of poly(vinylidene fluoride (or trifluoroethylene) with poly(methyl methacrylate) have been shown to be miscible over a wide phase composition. At 80% fluorocopolymer the blend exhibits a dielectric constant at 7.				
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POLYMER FILMS WITH ENHANCED DIELECTRIC PROPERTIES

FINAL REPORT

PROFESSOR JOHN R. REYNOLDS

July 26, 1993

U.S. ARMY RESEARCH OFFICE

DAAL03-90-G-0149

UNIVERSITY OF FLORIDA

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A. STATEMENT OF THE PROBLEM

Polymers, designed with high permittivities, low dissipation factors and high electric field breakdown strengths will find applications as dielectrics in capacitors and transmission lines to be used in communications equipment, computers and space power systems.^{1,2} Charge storage in polymer capacitors is controlled by the dielectric properties of the films employed. The total energy density that can be stored in a capacitor is directly proportional to the dielectric constant and the electric field breakdown strength squared. As an example, poly(vinylidene fluoride), and its derivatives, are known to exhibit the highest dielectric permittivity for commercially available polymeric materials and are quickly becoming useful in a number of applications.² This increase in permittivity allows a significant increase in energy density (energy stored per unit mass), a critical factor in all power systems. The polymers physical properties also strongly affect their applicability in charge storage. Films must be flexible and able to make good contact with metal electrodes over large surfaces. In addition, they must be mechanically strong and be thermally stable to melting and degradation. Pinholes and/or adhesive defects lead to low electric field breakdown strengths and thus processability and morphology are important considerations.

In this program, we have synthesized and investigated new dipole containing polymers with the ultimate goal directed to producing high quality dielectric polymer films with controllable dielectric properties. In addition to obtaining basic information on the reactivity of dipole containing monomers to copolymerization, the work was directed to preparing polymers with elevated dielectric constants and breakdown strengths, along with low dielectric loss. To accomplish this we also utilized copolymerization and polymer blending techniques to obtain multicomponent polymers whose properties might synergistically affect the electrical and physical properties of the final material.

B. SUMMARY OF IMPORTANT ACCOMPLISHMENTS

Within this program we addressed two main routes for the preparation of new high permittivity polymers for capacitor applications. These included the synthesis and polymerization

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of α -fluoroacrylonitrile along with miscible blend formation using the high permittivity copolymer poly(vinylidene fluoride-co-trifluoroethylene).

The following eleven major points serve as notable successes of the program:

- Improved high-yield syntheses of α -fluoroacrylonitrile and ethyl- α -fluoroacrylate have been developed yielding a dipole containing monomers in useful quantities (10-20 grams) as outlined in Scheme 1.
- Poly(α -fluoroacrylonitrile) (PFAN) has been synthesized, as outlined in Scheme 2, fully structurally characterized and shown to have a molecular weight on the order of $130,000 \text{ g mol}^{-1}$.
- Films of PFAN have been prepared by solution casting and exhibit relatively high dielectric permittivities of 8.9 at 50 Hz and 7.4 and 2.5 kHz.
- Poly(ethyl- α -fluoroacrylate) (PEFA) has been synthesized as outlined in Scheme 2, fully structurally characterized and shown to have a molecular weight (GPC determined) of $36,000 \text{ g mol}^{-1}$.
- Films of PEFA have been prepared by solution casting and exhibit lower dielectric permittivities (as expected) relative to PFAN of 4.0 at 50 Hz.
- Thermogravimetric analyses of PFAN and PEFA show the polymers to have onsets for decomposition of 200°C and 250°C respectively as shown in Figure 1 (Fig. 1A = PFAN, Fig. 1B = PEFA).
- Solution processing for film formation has been studied for the highest dielectric constant polymer (PFAN). Polymer films were cast from a number of solvents of ranging polarity. Cyclohexanone was found to yield the best free-standing films, but dielectric and thermogravimetric analyses indicated a significant amount of strongly bound solvent. A high vacuum/nitrogen flush method at elevated temperature was developed to remove this residual solvent. A film of PFAN prepared in this manner was submitted to the Army Laboratory ETDL (Dr. Michael Binder) for dielectric testing.

- Multiple copolymerizations were attempted with FAN in attempts to obtain copolymers with enhanced permittivities. The copolymerization behavior of FAN proved difficult to control.
- Blends of poly(vinylidene fluoride-co-trifluoroethylene) [P(VF₂/VF₃)] with poly(methyl methacrylate) (PMMA) have been shown to be miscible over a wide phase composition, incorporating PMMA into an amorphous fraction having a T_g dependent on composition.
- In these blends, dielectric permittivities remain relatively low at high PMMA concentrations where the films are completely amorphous ($\epsilon = 3-4$) as shown in Figure 2. At higher P(VF₂/VF₃) contents (>65%) ϵ' increases dramatically and a P(VF₂/VF₃) crystalline phase is observed. At 80% P(VF₂/VF₃) the permittivity increased to 7.
- Joint dielectric analyses were carried out with researchers at the U.S. Army ETDL. Results are summarized in Figure 3.

In summary, PFAN represents an interesting possibility as a new high permittivity polymer. Drawbacks to its use include a tedious multi-step monomer synthesis (12% overall yield based on starting reagents) and a relatively low thermal stability of the polymer. Future work in the preparation of alternating copolymers of the electron accepting FAN with electron donor monomers (e.g., vinyl ethers or 1,1-dialkoxyethenes) may prove interesting. Synthetic procedures will require development. Miscible blend formation of high permittivity polymers with low cost thermoplastics may prove useful in improving their processability and reducing cost of the overall material while retaining useful dielectric properties.

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C. LIST OF ALL PUBLICATIONS

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4. "Dielectric Analysis of Miscible Blends of Poly(vinylidene fluoride-co-trifluoroethylene) and Poly(methyl methacrylate)", J. R. Reynolds and E. Holloman, *Macromolecules*, manuscript in preparation.

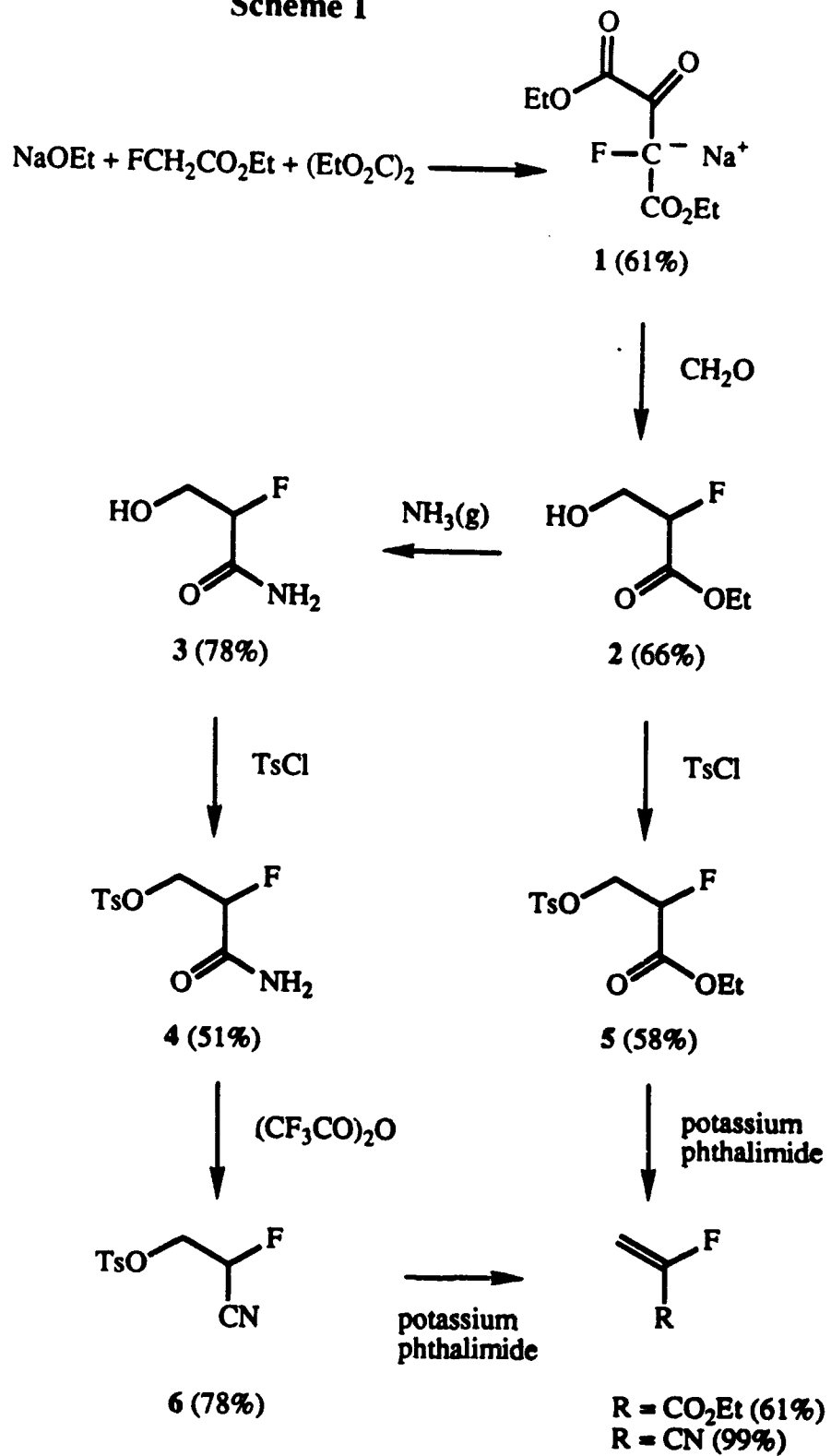
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REPORT OF INVENTIONS: None

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Scheme 1



Scheme 2

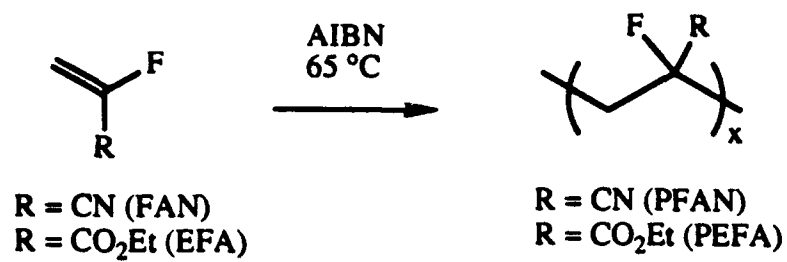


Figure 1

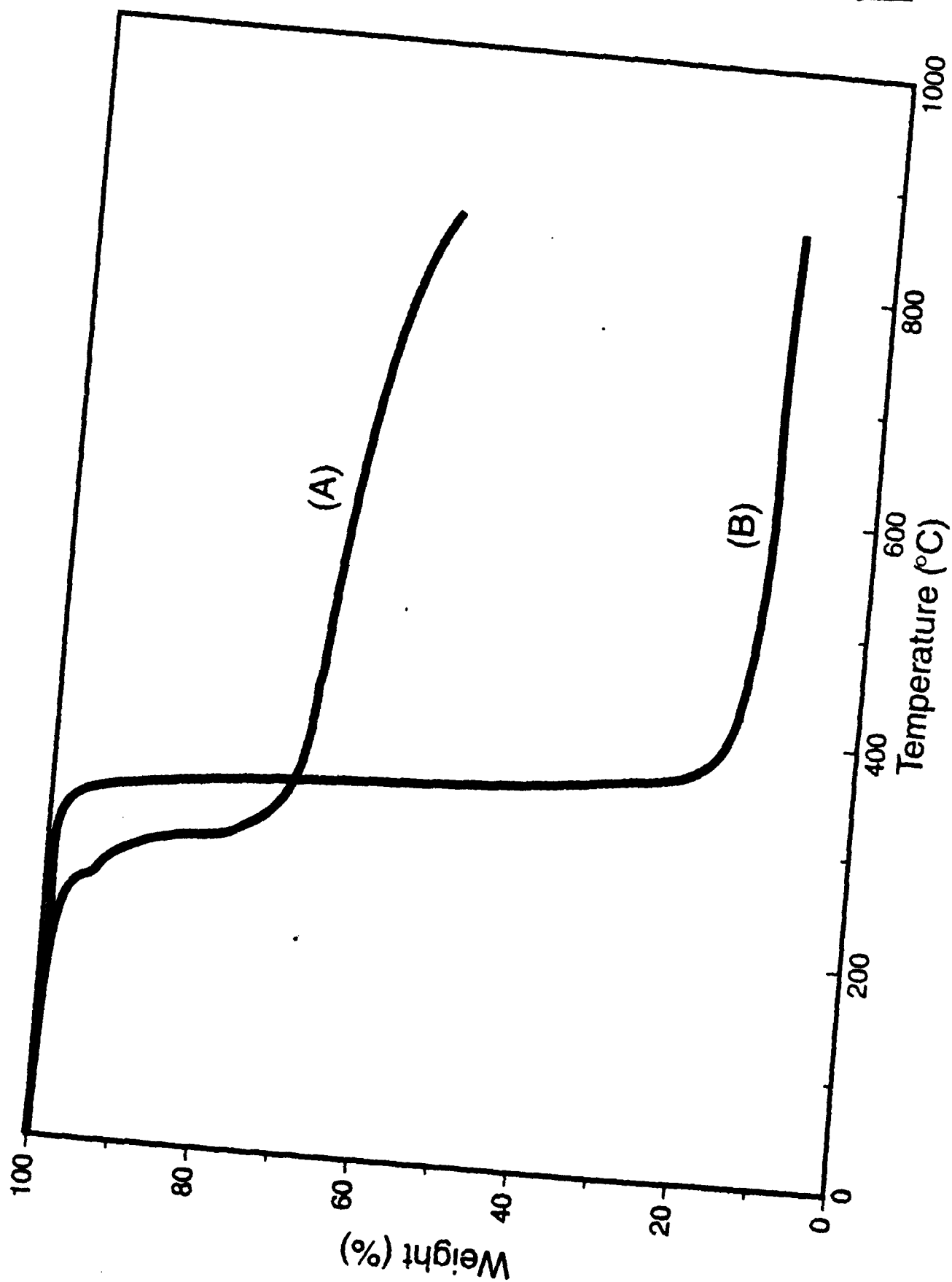
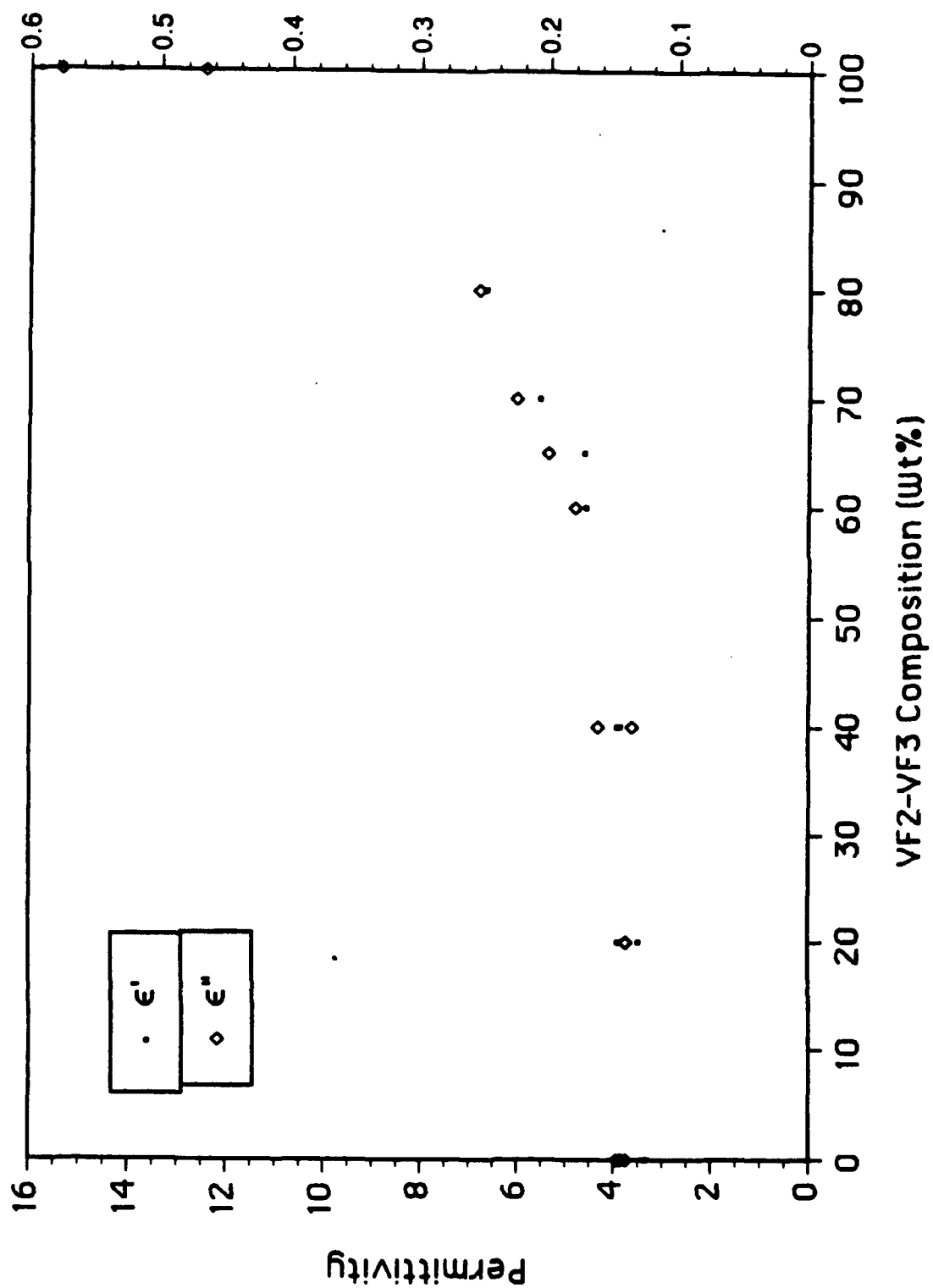


Figure 2



Dielectric Results of Polymer Films

Figure 3

(Results at 1 kHz)

Polymer	ETDL	E'	(E'')	UTA	E'	(E'')
PVDF		9.8	(.02)		10.3	(.25)
Polyimide (Kapton)		3.4	(.003)		3.8	(.24)
PFAN		4.4	(.04)		8.0	(.29)
(cast, no vacuum)						
PFAN		4.7	(.03)		---	(----)
(cast, vacuum)						
PFEA		3.4	(.04)		3.7	(.29)
Co PFAN/PFEA		3.73	(.03)		4.9	(.28)