linkage is formed simultaneously with the growth of the second block. Bulk copolymerizations were realized when the diphenylsiloxane compositions in the soft segment were greater than 50 wt %, while lower diphenylsiloxane compositions required a solvent to facilitate both the mixing and initial polymerization. DSC, DMTA, and SAXS results demonstrate that microphase-separated morphologies were achieved when diphenylsiloxane compositions in the soft segment were 50 wt % or less. The mechanical properties of the networks varied with the compositional changes in the soft segment.

Registry No. $(D_4)(D_4'')$(DGEBA) (block copolymer), 123380-81-4.

References and Notes

(1) Halpin, J. C. *Rubber Chem. Technol.* **1965**, *38*, 1007.
(2) Diament, Y.; Folman, M. *Polymer* **1979**, *20*, 1025.
(3) Gent, A. N.; Tompkins, D. A. *J. Polym. Sci., A-2* **1969**, *7*, 1483.
(4) Samuels, S. L.; Wilkes, G. L. *J. Polym. Sci., Polym. Symp.* **1978**, *43*, 149.
(5) Noolandi, J. *Polym. Eng. Sci.* **1984**, *24*, 70.
(6) Schollenberger, C. S.; Dinbergs, K. J. *Elastoplastics* **1979**, *11*, 58.
(7) Samuel, S. L.; Wilkes, G. L. *J. Polym. Sci.* **1971**, *11*(5), 369.
(8) Robeson, L. M.; Noshay, A.; Matzner, M.; Merriam, C. N. *Angew. Makromol. Chem.* **1973**, *29*(130), 47.
(9) Wilkes, G. L.; Moody, P. C.; Tant, M. R. *Polym. Eng. Sci.* **1979**, *19*, 1029.
(10) Hedrick, J. L.; Haidar, B.; Hofer, D. C.; Tran, C.; McGrath, J. E. *Polym. Prepr.* **1986**, *27*(2), 203.
(11) Hedrick, J. L.; Haidar, B.; Russel, T. P.; Hofer, D. C. *Macromolecules* **1987**, *21*, 1967.
(12) Hedrick, J. L.; Hofer, D. C.; Russell, T. P.; Haidar, B. *Polym. Bull.* **1988**, *19*, 573.
(13) Vonk, G. C. *J. Appl. Crystallogr.* **1971**, *47*, 340.
(14) Tobolsky, A. V.; McNight, W. J. *Polymeric Sulfur and Related Polymers*; Wiley: New York, 1975.
(15) Riffle, J. S.; Yilgor, I.; Tran, C.; Wiles, G. L.; McGrath, J. E. *Epoxy Resin-II*; Bauer, R. S.; ACS Symposium Series 221; Americal Chemical Society: Washington, DC, 1983; Chapter 2.
(16) Kantor, S. W.; Grubb, W. T.; Osthoff, R. C. *J. Am. Chem. Soc.* **1954**, *76*, 5190.
(17) Yilgor, I.; McGrath, J. E. *Adv. Polym. Sci.* **1988**, *86*, 1.
(18) Wnuk, A. J.; Davidson, T. F.; McGrath, J. E. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1978**, *34*, 89.
(19) Yilgor, I. et al. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*(1), 167.
(20) Tran, C. Ph.D. Thesis, Virginia Polytechnic Institute and State University, 1985.
(21) Yilgor, I.; Riffle, J. S.; Wilkes, G. L.; McGrath, J. E. *Polym. Bull.* **1982**, *8*, 535.
(22) Tyagi, D.; Wilkes, G. L.; Yilgor, I.; McGrath, J. E. *Polym. Bull.* **1982**, *8*, 543.
(23) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 3rd ed.; Clarendon: Oxford, 1975.

Synthesis and Characterization of the *tert*-Butyl Ester of the Oxydianiline/Pyromellitic Dianhydride Polyamic Acid

F. M. Houlihan,* B. J. Bachman, C. W. Wilkins, Jr., and C. A. Pryde

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974.

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ABSTRACT: Novel *tert*-butyl esters of oxydianiline/pyromellitic dianhydride polyamic acid were prepared in good yield. The polymers were prepared with either meta or para repeating units. The cure behavior of these *tert*-butyl esters was studied by IR, MS, and TG analysis and was compared to that of both the parent polyamic acid and its methyl ester. It was found that a rapid deprotection of the *tert*-butyl group occurs at around 200 °C with liberation of free polyamic acid. Consequently, the cure behavior at 200 °C of the *tert*-butyl ester approaches that of the parent polyamic acid. Furthermore, the isomerism of the repeating units does not appear to have any detectable effect on the cure behavior of the polymer, although meta isomerism appears to enhance solubility of the polymer in organic solvents.

Introduction

The lack of stability of polyamic acid solutions toward hydrolysis has been attributed to a catalytic effect engendered by the presence of an ortho carboxylic acid group.[1] Linear alkyl esters of polyamic acids[2-9] are much more hydrolytically stable in solution than the parent polyamic acids[3-8] and consequently show little change in molecular weight with time. This enhanced stability has been attributed to the blocking of the ortho carboxylic acid group by an ester group.[2] Unfortunately, the curing rates of linear alkyl esters are much slower than those of the corresponding free acids (up to 60 times slower for the *n*-butyl ester).[5] In our work we sought to avoid this difficulty by synthesizing a polyamic ester capable of thermally liberating the free polyamic acid. Moreover, it was hoped that this type of approach would yield novel polyimide precursors with thermally removable, bulky solubilizing groups. This could enable us to take advantage of the solubilizing effect of such groups during processing, giving access to low boiling point, film-casting solvents, while ensuring that the final cured polyimide retains valuable physical properties. This work reports the synthesis of the *tert*-butyl esters of the ODA/PMDA polyamic acids and describes some preliminary physical properties of these materials. The *tert*-butyl group (carbonate or ester) has been reported to thermally deprotect the hydroxyl group in styrene- and polycarbonate-based polymer systems.[10,11] This precedent encouraged us to choose this type of protecting group for our application. We chose to first study the *tert*-butyl ester of the polyamic acid derived from oxydianiline (ODA) and pyromellitic dianhydride (PMDA), because the simple alkyl esters (methyl, ethyl, propyl, butyl) of this polyamic acid have been prepared[5,6] and give a good basis for comparison.

Experimental Section

1. Materials and Characterization. Elemental analyses were obtained from Galbraith Laboratories, Inc. Polymer molecular weights were determined using a Waters Model 590 gel permeation chromatograph equipped with a Zorbax column, a Waters 410 differential refractometer, and a Waters Lambda-Max LC spectrophotometer. Molecular weights are given relative to polystyrene standards. NMR spectra were obtained on a JEOL

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90Q FTNMR spectrometer, IR spectra were obtained on a Digilab FTS-60 FTIR spectrometer, and mass spectra were obtained using an HP 5995C mass spectrometer with a direct insertion probe (DIP).

1.1. Preparation of the Di-*tert*-butyl Ester of Pyromellitic Acid. Potassium *tert*-butoxide, 20.60 g (184 mmol), was added, while stirring under dry argon, to 20.00 g (91.69 mmol) of pyromellitic dianhydride dissolved in 400 mL of THF. After stirring overnight the resulting suspension was filtered off, washed with THF and ether, and dried to give the potassium salt of the desired product. The salt was neutralized in aqueous solution with dilute HCl while keeping cold (10 °C). The product was filtered, washed with distilled water, dried, and recrystallized several times from ethanol/water. A total of 22.08 g (66% yield) of di-*tert*-butyl ester was recovered in three crops of crystals. These crops consisted of 10.50 g of pure para isomer, 7.43 g of pure meta isomer, and a 50% mixture of the two isomers that constituted the remainder.

Meta Isomer. Elemental analysis (C, H, O): found (58.98, 6.10, 35.29); calc (59.01, 6.05, 34.93). IR (KBr, cm^{-1}): 3415 (O–H str, acid); 2987, 2941 (C–H str, *tert*-butyl); 1704 (C=O str, acid, ester); 1502 (C=C str); 1442 (CH$_3$ antisym deformn); 1412; 1394, 1310 (*tert*-butyl sym deformn, CH$_3$ rock); 1276 (C–O–C str, ester); 1260 (*tert*-butyl-coupled CH$_3$ rock); 1163, 1137, 1112 (C–O str); 927 (*tert*-butyl-coupled CH$_3$ rock); 848, 796, 778 (CH out of plane aromatic). ^{1}H NMR (ppm, DMSO-d_6); for assignments see Scheme I): 13.64 (br s, 2 H, OH acid); 8.05 (s, 1 H, CH-6); 7.81 (s, 1 H, CH-3); 1.65 (s, 18 H, CH$_3$ *tert*-butyl). ^{13}C NMR (ppm, DMSO-d_6); for assignments see Scheme I): 167.01 (s, C=O acid); 165.12 (s, C=O ester); 135.70 (s, C-1,5); 133.81 (s, C-2, C-4); 129.10 (d, C-3); 27.96 (d, C-6); 82.56 (s, C, *tert*-butyl); 27.41 (t, CH$_3$ *tert*-butyl).

Para Isomer. Elemental analysis (C, H, O): found (58.87, 6.04, 34.79); calc (59.01, 6.05, 34.93). IR (KBr, cm^{-1}): 3570 (O–H str, acid); 3001 (C–H str, aromatic); 2982, 2935 (C–H str, *tert*-butyl); 1728 (C=O str, ester); 1704 (C=O str, ester); 1502 (C=C str, ester); 1442; 1422 (CH$_3$ antisym deformn), 1369, 1306 (*tert*-butyl sym deformn, CH$_3$ rock); 1280 (C–O–C str, ester); 1266, 1259 (*tert*-butyl-coupled CH$_3$ rock); 1177, 1142 (C–O str); 917 (*tert*-butyl-coupled CH$_3$ rock); 850, 803 (CH out of plane aromatic). ^{1}H NMR (ppm, DMSO-d_6; for assignments see Scheme I): 1364 (br s, 2 h, OH acid); 7.93 (s, 2 H, CH-6, CH-3); 1.65 (s, 18 H, CH$_3$ *tert*-butyl). ^{13}C NMR (DMSO-d_6; for assignments see Scheme I): 167.01 (s, C=O acid); 165.12 (s, C=O ester); 135.05 (s, C-4, C-1); 134.46 (s, C-5, C-2); 128.50 (d, C-6, C-3); 82.56 (s, C *tert*-butyl); 27.41 (t, CH$_3$ *tert*-butyl).

1.2. Preparation of Dimethyl Ester of Pyromellitic Acid. In a 200-mL flask 12.16 g (55.7 mmol) of pyromellitic dianhydride was slowly dissolved with gentle heating in 60 mL of dry methanol under dry nitrogen. After the reaction was complete, as indicated by dissolution of pyromellitic dianhydride, the solution was cooled and 150 mL of distilled water was added. The methanol was removed under vacuum until crystallization was initiated. After overnight refrigeration, the crystals were filtered and dried under vacuum at 40 °C. In this way 5.0 g (32% yield) of the pure *p*-dimethyl ester of pyromellitic acid were isolated. This material had spectral properties consistent with those reported in the literature.[5,6,8]

1.3. Preparation of Di-*n*-butyl Ester of Pyromellitic Acid. The synthesis of the di-*n*-butyl ester is the same as that for dimethyl ester described above, except that *n*-butyl alcohol was used instead of methanol. The yield of ester is 60%. This material had spectral properties consistent with those reported in the literature.[5]

1.4. Formation of the Polyamic Acid Ester Derived from the *p*-Di-*tert*-butyl Ester of Pyromellitic Acid and ODA in NMP. A solution was prepared under argon consisting of 0.7327 g (2 mmol) of *p*-di-*tert*-butyl ester of PMDA, 0.4005 g (2 mmol) of ODA, and 0.56 mL of triethylamine in solution in 2 mL of NMP. The solution was cooled to −10 °C and 1.6976 g (4 mmol) of *N,N′*-(phenylphosphino)bis[2(3*H*)-benzothiazolone] was added slowly. The reaction was kept at −10 °C for 12 min and then allowed to return to room temperature and stirred for 2 h more. After diluting with 8 mL of NMP, the polymer solution was precipitated in 200 mL of methanol, filtered, washed with methanol, and dried under vacuum for several days. In this way 0.83 g (79% yield) of tan polymer was isolated. Molecular weight: $M_w = 18\,000$, $M_n = 11\,000$, $D = 1.6$. Elemental analysis (C, H, N, O): found (66.56, 5.88, 5.30, 21.50); calc (67.91, 5.69, 5.27, 21.10). IR (KBr, cm^{-1}): 3320 (N–H str, amide); 1722 (C=O str, ester); 1679 (C=O str, amide); 1607 (C–N, N–H coupled deformn); 1512 (C=C str); 1407, 1391 (*tert*-butyl sym, out of plane CH$_3$ rock); 1220, 1249 (*tert*-butyl-coupled CH$_3$ rock); 1162, 1135, 1106 (C–O–C sym deformn, ester). ^{1}H NMR (DMSO-d_6, ppm; for assignments see Figure 1b): 10.63 (br s, 2 H, amide); 7.93 (s, 2 H, H-6); 7.78 (d, 4 H, H-2); 7.04 (d, 4 H, H-3); 1.49 (s, H-11). ^{13}C NMR (DMSO-d_6, ppm); for assignments see Figure 1b): 165.17 (s, C-9); 164.42 (s, C-8); 152.66 (s, C-4); 138.74 (s, C-5); 134.78 (s, C-1); 133.26 (s, C-7); 128.50 (d, C-6); 120.97 (d, C-2); 118.69 (d, C-3); 82.23 (s, C-10); 27.35 (q, C-11).

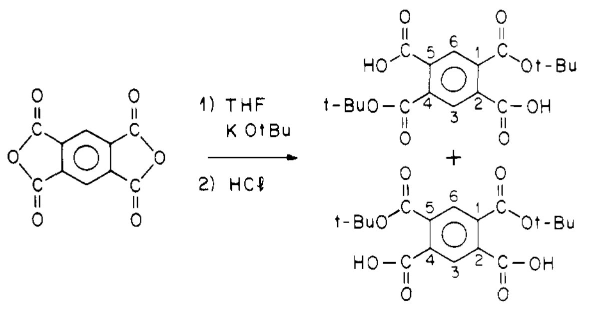
1.5. Formation of the Polyamic Acid Ester Derived from the *m*-Di-*tert*-butyl Ester of Pyromellitic Acid and ODA in NMP. The procedure was the same as in section 1.2 except that the *m*-di-*tert*-butyl ester of PMDA was used as a starting material. The workup differed in that the polymer was precipitated in a 50/50 mixture of methanol and water. In this way 0.87 g (82% yield) of tan polymer was recovered. Molecular weight: $M_w = 20\,000$, $M_n = 7000$, $D = 2.8$. Elemental analysis (C, H, N, O): found (66.63, 5.55, 5.22, 21.65); calc (67.91, 5.69, 5.27, 21.10). IR (KBr, cm^{-1}): 3320 (N–H str); 1722 (C=O str, ester); 1685 (C=O str, amide); 1605 (C–N, N–H coupled deformn); 1407, 1392 (*tert*-butyl sym, out of plane CH$_3$ rock); 1497 (C=C str); 1229, 1251 (*tert*-butyl-coupled CH$_3$ rock); 1159, 1133, 1109 (C–O–C sym deformn). ^{1}H NMR (DMSO-d_6, ppm); for assignments see Figure 1a): 10.62 (br s, 2 H, amide); 8.13 (s, 1 H, H-8); 7.78 (d, 4 H, H-2); 7.60 (s, 1 H, H-6); 7.04 (d, 4 H, H-3); 1.43 (s, 18 H, H-12). ^{13}C NMR (DMSO-d_6, ppm; for assignments see Figure 1a): 165.17 (s, C-10); 164.31 (s, C-9); 152.66 (s, C-4); 140.47 (d, C-5); 134.78 (d, C-1); 131.53 (d, C-7); 130.07 (d, C-6); 127.47 (d, C-8); 120.98 (d, C-2); 118.69 (d, C-3); 82.12 (s, C-11); 27.35 (q, C-12).

1.6. Formation of the Polyamic Acid Ester Derived from the *p*-Di-*tert*-butyl Ester of Pyromellitic Acid and ODA in THF. A suspension was prepared under argon consisting of 0.7327 g (2 mmol) of the diacid, 0.4005 g (2 mmol) of 4-aminophenyl ether, 0.56 mL of triethylamine in 2 mL of dry THF. This suspension was cooled to −10 °C, and 1.6976 g (4.0 mmol) of *N,N′*-(phenylphosphino)bis[2(3*H*)-benzothiazolone] was added slowly with stirring using a powder dropping funnel. After this addition, the suspension was stirred at this temperature for 12 min. The reaction mixture was then allowed to return to room temperature. After stirring for 10–20 min, a clear yellowish solution was obtained, which quickly thickened. After 1 h, the solution was so thick that stirring stopped. The thick gel was broken up, suspended in 20 mL of THF, and precipitated into 400 mL of methanol. The white powder thus formed was filtered and washed with several aliquots of methanol. The material was extracted overnight with refluxing THF in a Soxhlet. After the material was dried overnight at room temperature under vacuum, 0.8533 g of a tan powder was obtained, giving an 81% recovered yield. The spectral characteristics of this material are the same as those of the polymer isolated in section 1.4. Molecular weight: $M_w = 34\,000$, $M_n = 17\,000$, $D = 2.0$.

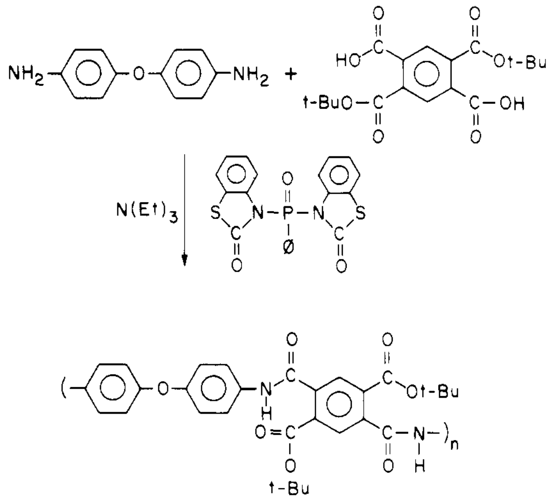
1.7. Formation of the Dimethyl Ester and Di-*n*-butyl Esters of the Polyamic Acid Derived from PMDA and ODA. The procedures used for these two esters are the same as described in section 1.4 except the dimethyl ester or the di-*n*-butyl of pyromellitic acids was that used in the synthesis. The yields are, respectively, 84% and 79%. The products' spectral properties were consistent with those reported in the literature.[5,6,8]

2. Studies of Polymer Cure. The mass spectral curing studies were done by heating each sample of polymer in the DIP consecutively at 100, 200, and 350 °C for 1 h each. The extent of cure at 200 °C was estimated by taking the ratio of the area for the peak at 200 °C in the TIC (or the ion chromatogram of water or isobutene) to the combined area of the peaks at 200 and 350 °C. The samples for the IR curing study were spun from dimethylacetamide solutions of the polyamic acid or its esters onto NaCl plates. The spun samples were dried at 110 °C for about 1 h, heated slowly to the cure temperature, allowed to remain at that temperature for 1 h, and then cooled. The degree of imidization then was calculated from the 1375-cm^{-1} imide peak (C–N str) using the 1501-cm^{-1} band (aromatic ring breathing) as an

Scheme I



Scheme II



internal standard.[11] Thermogravimetry (TG) curing studies were performed on a Perkin-Elmer TGS-2 thermogravimetric analyzer interfaced with a System 4 microprocessor for temperature programming and a TADS Model 3700 data station for data acquisition and operational control. All measurements were obtained in N_2 with a gas-flow rate of 30 cm^3/min. Heating rates used for the dynamic study were 5 and 25 °C/min.

Results and Discussion

1. Materials. The synthetic pathway to arrive at the di-*tert*-butyl esters of pyromellitic acid is shown in Scheme I. These esters could not be made by the classical pathway used for the diester derived from linear alcohols.[9] The synthesis of the polyamic acid esters was accomplished by a procedure involving a direct coupling of a diester diacid monomer with an aromatic diamine (Scheme II). A peptide-coupling agent (*N*,*N*′-(phenylphosphino)bis[2-(3*H*)-benzothiazolone]), reported useful in the synthesis of aromatic polyamides,[13] was used in this reaction. This approach not only had the advantage of avoiding conditions that would cleave the *tert*-butyl ester but also decreased the number of steps needed to prepare the polymer. The polymerization with ODA was done with both the meta and para isomers of the diacid diester, and the solvents used were either NMP or THF. The yield of polymer ranged from 78 to 81%.

The *tert*-butyl esters of ODA/PMDA polyamic acid retained the meta or para isomerism of the parent di-*tert*-butyl ester diacid even on prolonged storage in DMSO solution. The identification of the isomers was based on the data provided by ^{13}C and ^1H NMR spectra. Parts A and B of Figure 1 show the two distinct ^{13}C NMR spectra given by the meta and para isomers. The polymer made up of meta units is soluble in low-boiling solvents such as THF or glyme. In contrast, the polymer consisting of para units is soluble only in high-boiling, polar solvents such as DMF and NMP. This difference in solubility cannot be accounted for by differences in molecular weight since the two polymers have similar molecular weights. This drastic difference in solubility between para and meta isomers of polyamic acid esters is characteristic of many other types of polymers and is due to the fact that the meta geometry tends to hinder packing of polymer molecules far more than the para geometry. In the case of our materials this packing difficulty may be accentuated by the steric bulk of the *tert*-butyl group and its ability to disrupt interchain interactions. It has also been found that only partial meta isomerism (70%) is enough to give to or result in solubility (up to at least 50% wt) of the polymer in low boiling point, film-casting solvents. The same procedure was also extended to the *n*-butyl and methyl ester of the ODA/PMDA polyamic acid, giving 79% and 84% yield, respectively.

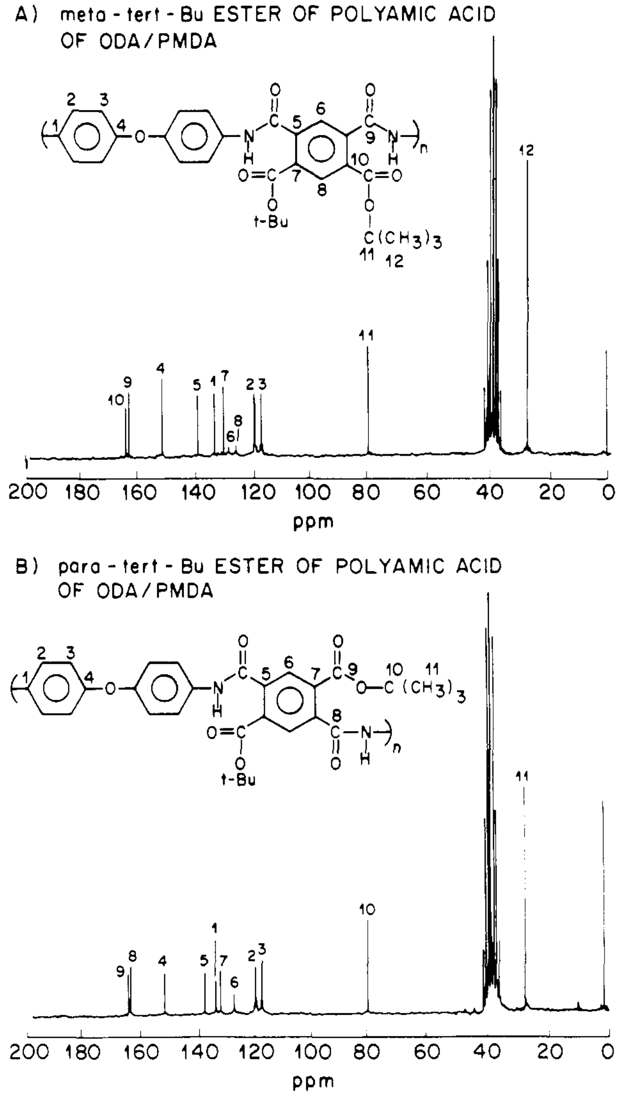


Figure 1. ^{13}C NMR spectra of the two isomers of the *tert*-butyl ester of the ODA/PMDA polyamic acid.

2. Curing Behavior of Polymers. Conformational studies of the imidization of ODA/PMDA polyamic acid have suggested that the ratio of para and meta isomers may play an important part in the reaction kinetics of imidization.[14] Specifically, it was predicted that pure para isomerism should lead to 100% imidization, while in the case of meta isomerism, 18% of the total polymer conformations should require major steric rearrangement to permit full imidization.[14] Since our polymers should, in theory, permit the formation of a free polyamic acid with an initially pure meta or para isomerism, we wished to see

Table I
TG Analyses of ODA/PDA Polyamic Acid and Its Esterified Products

polymer	heating rate, °C/min	condition	onset temp, °C	max rate of reaction, °C	wt loss (theory), %	wt loss (actual), %
ODA/PMDA	25	solvent	153	202	8.61	23.9
p-tert-butyl ester	25	solvent	183	197	27.9	28.3
m-tert-butyl ester	25	solvent	173	190	27.9	30.0
p-tert-butyl ester	5	solvent	164	178	27.9	28.6
m-tert-butyl ester	5	solvent	155	167	27.9	30.0
ODA/PMDA	5	solvent removed	150	187	8.61	13.1
p-tert-butyl ester	5	solvent removed	163	178	27.9	27.2
m-tert-butyl ester	5	solvent removed	164	202	27.9	28.3
methyl ester	5	solvent removed	176	217	15.3	16.9
n-butyl ester	5	solvent removed	193	247	27.9	29.0

if we could observe any difference in the extent of imidization for the two isomeric polymers. Moreover, it was also of interest for us to see if the protection of the polyamic acid group with the *tert*-butyl group had any drastic lowering effect on the curing rate as had been observed in case of the *n*-butyl ester[5] and to verify that the products given off during imidization were indeed isobutene and water and not *tert*-butyl alcohol.

2.1. Thermogravimetric Analysis. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves obtained using a heating rate of 25 °C/min for ODA/PMDA polyamic acid and its esterified meta and para isomeric products are shown in Figure 2. It can be seen that the ODA/PMDA polyamic acid TG curve (Figure 2) has a broader region for weight loss. Figure 2 also shows the asymmetric-shaped DTG curves for the isomeric esters compared with the symmetric curves obtained for the polyamic acid. Additionally, the maximum rate of reaction can be seen to occur earlier for the isomeric esters than for the polyamic acid. The asymmetric-shaped DTG curves for the *tert*-butyl ester could be explained by the presence of two simultaneously occurring reactions, namely, the deprotection of the carboxylic acid *tert*-butyl group, which gives isobutene, and the imidization reaction, which generates water.

Table I summarizes the maximum rate of reaction, onset temperature, and weight loss percent at 495 °C for the ODA/PMDA polyamic acid as well as the para and meta isomers of the esters. Additionally, a comparison of data obtained with and without solvent removal is provided.

The theoretical weight loss from the elimination of water, shown in Table I, is 8.61% for ODA/PMDA polyamic acid. Contrast this with the actual weight loss obtained before and after solvent removal/drying of 23.9% and 13.1%, respectively. Although there were heating rate differences, the ODA/PMDA polyamic acid still exhibited a larger weight loss value before and after extraction/drying than predicted from the theoretical value.

Solvation of the polyamic acid by NMP could account for these larger weight losses. Conversely, both isomeric polyamic acid esters approached their theoretical weight loss of 27.9% regardless of solvent removal procedures.

The *p*-methyl diester of ODA/PMDA had a weight loss of 16.9% at 495 °C compared to the theoretical value of 15.3%. Onset of weight loss for this polymer at a heating rate of 5 °C/min was 177 °C with a maximum rate of reaction at 217 °C. As was the case for the polyamic acid samples, the DTG for this polymer is symmetric. The methyl ester has a higher onset and maximum rate of reaction when compared to ODA/PMDA polyamic acid and its *tert*-butyl esters, indicating that the *tert*-butyl ester falls between ODA/PMDA polyamic acid and its methyl ester in ease of imidization. Since earlier work[5] had indicated that the *n*-butyl ester was far less susceptible to imidization than the methyl ester, this is a strong indication that the reaction does not proceed by the elimination of *tert*-butyl alcohol, since this process should be even harder to achieve than the elimination of *n*-butyl alcohol. Indeed, a TGA (5 °C/min) of a sample of the *n*-butyl ester confirmed that this material had a higher onset (193 °C) and maximum rate of reaction than either the methyl or *tert*-butyl ester. Figure 3 shows an isothermal TGA study, which illustrates the drastic difference in the imidization rates for the *tert*-butyl ester and the *n*-butyl ester. In this study a sample of polymer was heated at three temperatures (100, 200, and 400 °C) for 1 h at each temperature. By comparing the weight loss at 200 °C to that at the final cure temperature, we could calculate the percent imidization. Thus the *n*-butyl ester was found to have a much

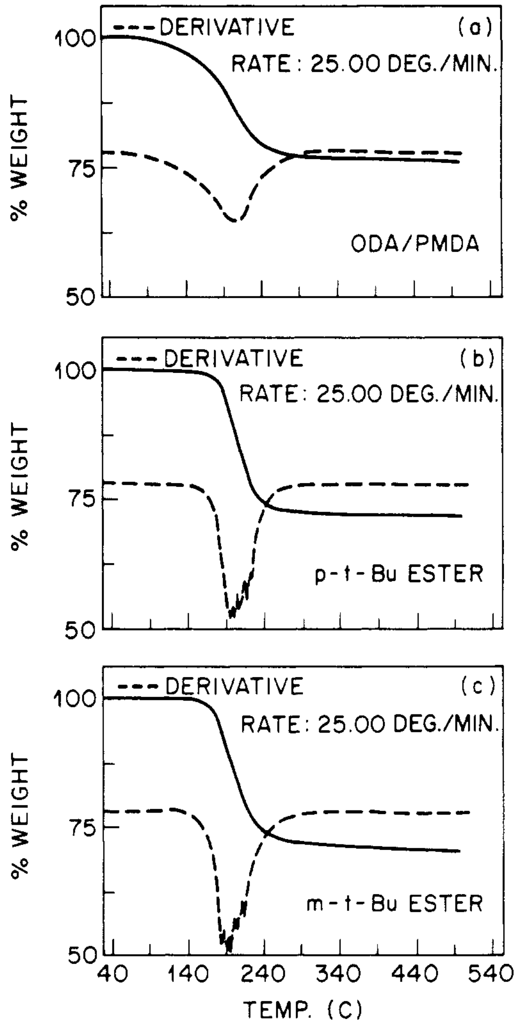


Figure 2. TG and DTG curves for the ODA/PMDA polyamic acid and the two isomers of *tert*-butyl ester.

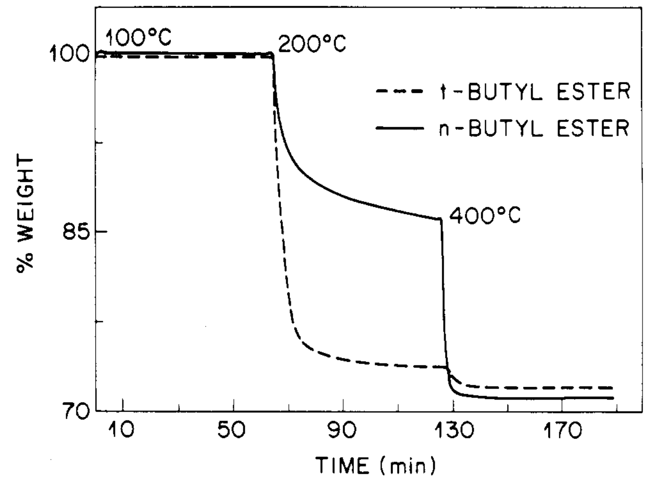


Figure 3. Isothermal TG study of the imidization of *tert*-butyl and *n*-butyl esters of the ODA/PMDA polyamic acid.

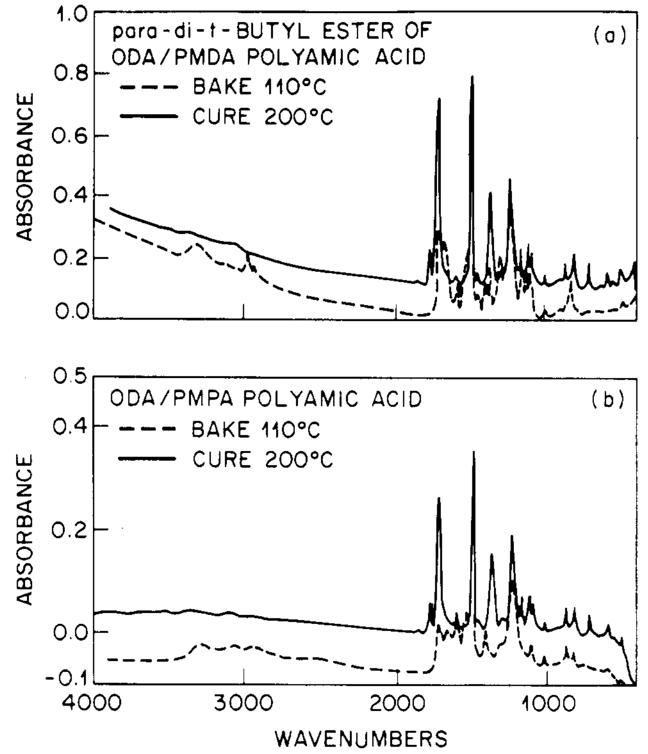


Figure 4. IR spectra for curing of ODA/PMDA polyamic acid and its *tert*-butyl ester.

lower percent imidization (46%) than was found for the *tert*-butyl ester (93%).

2.2. IR Spectroscopy. In this study the degree of imidization was determined from the 1375-cm^{-1} imide peak using the 1501-cm^{-1} band as an internal standard.[12] A preliminary study, which involved comparing samples heated to 200 °C for 1 h, indicated no significant differences in cure for either of the two esters as compared to PMDA/ODA polyamic acid: Analysis of all three samples indicated 81 ± 2% imidization, based on results for a sample given a final cure of 400 °C. Further comparisons between the polyamic acid and the para ester at a higher cure temperature (250 °C) showed exactly the same degree of cure (96% conversion to imide) for the two samples. Immediately after spinning, the film of the para ester became opaque, suggesting possible crystallization. This did not occur in the case of the meta isomer. This behavior would be in line with the differences in molecular shape discussed previously.

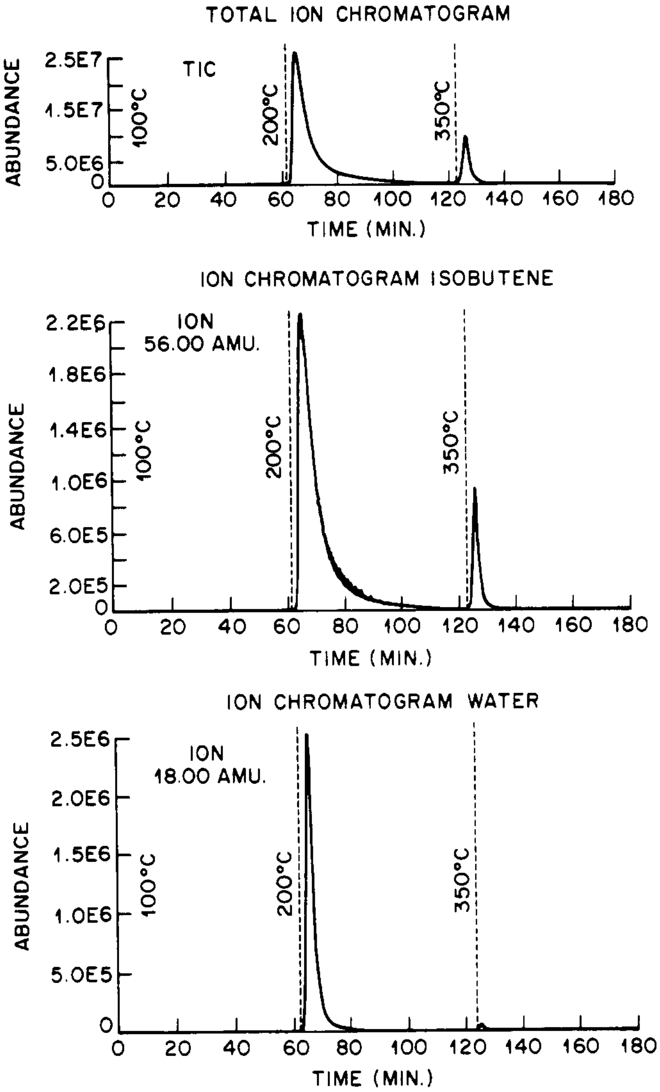


Figure 5. Total ion chromatogram and ion chromatograms for isobutene and water taken during the curing of the para isomer of the *tert*-butyl ester of the ODA/PMDA polyamic acid.

The opacity the film formed from the para isomer was maintained through heating to 300 °C. For both esters loss of the *tert*-butyl group appears to essentially complete by 200 °C. The bands in the 2850–3000-cm^{-1} region attributable to the CH_3 are gone, and the spectra (parts a and b of Figure 4) show no other obvious differences. The samples prepared from both the esters and the polyamic acid show the characteristic anhydride peak near 1860 cm^{-1}.

2.3. Mass Spectroscopic Analysis. Samples of ODA/PMDA polyamic acid, the methyl ester, and the meta and para isomers of the *tert*-butyl ester were baked at 100 °C for 1 h to remove solvent or water. They were then cured at 200 °C for 1 h followed by a final cure at 350 °C to near complete imidization.

2.3.1. Curing of *tert*-Butyl Ester Polymers. Mass spectroscopy showed that the products given off during the cure cycle were water and isobutene and not *tert*-butyl alcohol. The cure can be followed in three ways: The total ion chromatogram (TIC) can be examined or, alternatively, the evolution of water and isobutene can be monitored separately by looking at the ion chromatogram of each molecular species (m/e 18 and 56). As can be seen in Figure 5, which depicts the ion chromatogram for water and isobutene given off during the curing of the *p*-*tert*-butyl ester, the liberation of water and isobutene occurs

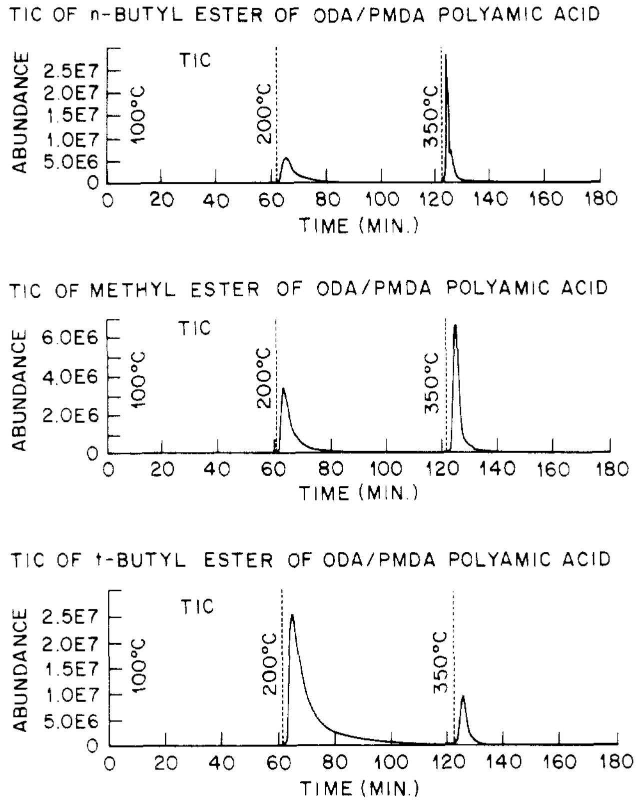


Figure 6. Total ion chromatograms taken during the curing of the *tert*-butyl, *n*-butyl, and methyl esters of the ODA/PMDA polyamic acid.

simultaneously. Heating samples of the *tert*-butyl esters of the ODA/PMDA polyamic acid for 1 h at temperatures ranging up to 150 °C does not cause any reaction to occur. This is a strong indication that in order to effect cure in these polymers the temperature for the thermal deprotection of the *tert*-butyl ester must be attained. Suprisingly, it is seen that isobutene is still being given off at 350 °C, indicating that all the protecting groups were not removed by heating at 200 °C for 1 h. This is an indication that under these conditions the removal of the *tert*-butyl protecting group may be the rate-determining step. The extent of cure at 200 °C is estimated by taking the ratio of the area for the peak at 200 °C in the TIC (or the ion chromatogram of water or isobutene) to the combined area of the peaks at 200 and 350 °C. In this way it is found that cure occurs to the extent of 87% when heating at 200 °C for 1 h. When the same calculation is used, the ion chromatogram of the molecular ion of isobutene (*m*/*e* 56) gives a percent imidization of 88%. However, the ion chromatogram for the molecular ion of water (*m*/*e* 18) gives a somewhat higher estimate of percent imidization (97%). This difference might be a consequence of a lack of sensitivity of the detector of the instrument in a region so close to its lowest mass limit (*m*/*e* 10). The meta isomer gave no detectable difference in curing behavior. The percent imidization for the *tert*-butyl ester of ODA/PMDA polyamic acid calculated by the IR study (81%) is close to that estimated by mass spectroscopy (87%). The difference between the two values appears to be mostly due to the fact that the IR results are based on a final cure at 400 °C. Although a cure to 350 °C does not afford complete imidization, it represents the highest temperature accessible using the DIP attachment on the mass spectrometer. When the IR results are recalculated using a cure at 350 °C as a final cure, instead of 400 °C, a result of 88% is found, which is virtually identical with the result found by mass spectroscopy. Because isobutene is still being evolved during the 400 °C cure, the removal of the *tert*-butyl group may be the rate-determining step; however, since we have already found that the percent imidization, as estimated by IR spectroscopy, is identical for the polyamic acid and its *tert*-butyl ester, it would appear that the deprotection reaction is still rapid enough not to hinder significantly the effective percent imidization at 200 °C.

2.3.2. Curing of Methyl and *tert*-Butyl Esters. As can be seen by the TIC for the *n*-butyl ester (Figure 6), it undergoes much less curing (43%) than the *tert*-butyl ester. This confirms the same trend that was observed in the isothermal TGA study where a 46% cure was found. Even the methyl ester (Figure 6), which is expected to give the highest cure rate for a linear ester, gives only 52% cure. As expected, the products given off during the cure of the esters of the linear alcohols are the corresponding linear alcohols.

3. Conclusions. We have shown that *tert*-butyl esters of polyamic acids can be prepared in good yield and with acceptable molecular weights. The reaction has also been extended to other esters. Moreover, the *tert*-butyl esters can be prepared as pure meta or para polymers, which show distinct differences in solubility. It has also been found by IR spectroscopy that the extent of cure of the *tert*-butyl esters at a given temperature is nearly the same as that for the free polyamic acid. This indicates that the deprotection of the acid group is very rapid and does not hinder significantly the cyclization of the polyamic acid. The isomerism of the *tert*-butyl ester does not appear to have any great effect on the cyclization reaction or cyclization to imide as was established by curing studies done by IR spectroscopy, mass spectroscopy, and TG analysis. Studies by mass spectroscopy have confirmed that the products given off during the cure of the *tert*-butyl esters are isobutene and water. This confirms that the cyclization of the *tert*-butyl ester proceeds by a more facile mechanism involving the liberation of a free polyamic acid rather than by a thermal elimination of alcohol. The linear esters gave off linear alcohols during cure and were seen to have slower rates of imidization at 200 °C than the *tert*-butyl esters.

In future work the curing behavior of these material will be examined in more detail to determine the rate constants for cure and to compare these to those reported in the literature for polyamic acids and *n*-alkyl esters of polyamic acids. The more detailed study will allow us to determine if indeed the meta and para esters have identical curing behavior, or if, as predicted elsewhere,[14] there are differences. Other bulky protecting groups capable of thermal removal will also be investigated. Polymers with varying ratios of meta and para repeating units will also be prepared to investigate the effect this has on solubility.

References and Notes

(1) Frost, L. W.; Keese, I. I. *Appl. Polym. Sci.* **1964**, *8*, 1039.
(2) Kharkov, S. N.; Vinogradova, S. V.; Vygodskii, Y. S.; Gerashchenko, Z. V. *Vysokomol. Soyed.* **1971**, *A13*, 1190.
(3) Kharkov, S. N.; Krasnov, Ye P.; Lavrova, Z. N.; Baranova, S. A.; Aksevova, V. P.; Chegolya, A. S. *Vysokomol. Soyed.* **1971**, *A13*, 833.
(4) Molodtsvova, Y. D.; Timofeyeva, G. I.; Pavlova, S. S. A.; Vygodski, Y. S.; Vinogradova, S. V.; Korshak, V. V. *Vysokomol. Soyed.* **1977**, *A19*, 346.
(5) Nishizaki, S.; Moriwaki, T. *Kogyo Kagaku Zasshi* **1970**, *73*, 1873.
(6) Nishizaki, S.; Moriwaki, T. *Ind. Chem. Mag.* **1968**, *71*, 1559.
(7) Kudryavtsev, V. V.; Koton, M. M.; Meleshko, T. K.; Sklizkova, V. P. *Vysokomol. Soyed., Ser. A* **1975**, *A17*, 1764.
(8) Koltsov, A. I.; Dauengauer, S. A.; Denisov, V. M.; Shibaev, L. A.; Sazanov, Yu N.; Bukina, M. K.; Koton, M. M. *Dokl. Akad. Nauk SSSR* **1984**, *B278*, 1380.

(9) Bessonov, M. I.; Koton, M. M.; Kudryavtsev, V. V.; Laius, L. A. *Polyimides—Thermally Stable Polymers*; Plenum Press: New York, 1987.
(10) Frechet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer* **1983,** *24,* 995. Ito, H.; Willson, C. G.; Frechet, J. M. J.; Farrall, M. J.; Eichler, E. *Macromolecules* **1983,** *16,* 510. Proceedings SPIE Conference, Santa Clara, 1987. Ito, H.; Willson, C. G.; Frechet, J. M. J. US Patent 4,491,628, 1985.
(11) Frechet, J. M. J.; Buchard, F.; Eichler, E.; Houlihan, F. M.; Izawa, T.; Kryozka, B.; Willson, C. G. *Polym. (Tokyo)* **1987,** *19,* 31.
(12) Pryde, C. A., *J. Polym. Sci., Part A: Polym. Chem.*, in press.
(13) Ueda, M.; Mochizuki, A.; Hiratsuka, I.; Oikawa, H. *Bull. Chem. Soc. Jpn.* **1985,** *58,* 3291.
(14) Milevshaya, I. S.; Lukasheva, N. V.; Yel'yashevich, A. M. *Vysokomol. Soyed., Ser. A* **1979,** *A21,* 1302.

Dielectric Relaxation Studies of Ion Motions in Electrolyte-Containing Perfluorosulfonate Ionomers. 4. Long-Range Ion Transport

K. A. Mauritz

Department of Polymer Science and Department of Physics, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076. *Received February 28, 1989; Revised Manuscript Received May 8, 1989*

ABSTRACT: Mauritz and co-workers have shown that the dielectric loss spectra in the low frequency (ω) region of Nafion sulfonate membranes incorporating aqueous electrolytes vary as ω^{-n} where $0 < n < 1$. A more detailed examination of n for selected systems reveals that this power is a distinct function of mobile ion type, ionic concentration, and system temperature. While we had earlier attributed this power law behavior, in general, to long-range, i.e., intercluster, ion motions, we have attempted herein to more carefully analyze this phenomenon in terms of (a) the related theories of processes that are fractal in space and time, (b) the theory of the dispersive transport of charge carriers in amorphous materials, and (c) the cluster theory of the anomalous low-frequency dielectric dispersion phenomenon. While all these models presently lack strong microstructural specificity, it is nonetheless felt that their refinement would allow for experimentally extracted values of n to be used as a rough qualitative index of morphological regularity or "texture" over an array of ionic clusters or as a quantitative measure of the degree of connectivity or tortuosity of the overall charge network.

Introduction

Mauritz et al. have recently communicated the results of detailed dielectric relaxation analyses of perfluorosulfonate membranes that were imbibed with a variety of aqueous electrolytes at various fixed temperatures over the frequency ($f = \omega/2\pi$) range 5 Hz to 13 MHz as a function of electrolyte concentration.[1-3] Our main goal throughout these studies has been a rationalization of the structures and characteristic motions of hydrated ions within the established clustered morphology of these ionomers, particularly in the realm of high ion concentrations. To be sure, there is a critical need to understand and control these motions from the standpoint of selective molecular transport across these membranes in the industrial arena of separations technology. On the other hand, from a fundamental scientific perspective, we are aware that little, at this time, is actually understood of the physics of concentrated electrolytes in the bulk, not to mention their being incorporated within a highly interactive ionomeric system possessing structural heterogeneity at the 50-Å level. The distinct hydrophilic/hydrophobic phase-separated morphology of perfluorosulfonate membranes offers an ordered matrix throughout which electrolytes can be finely dispersed so as to generate extraordinarily high surface-to-volume ratios for these sorbed solutions. Necessarily, a considerable fraction of the ions and water molecules incorporated within the approximately 40-Å diameter polar clusters must reside at the hydrophilic/hydrophobic interface and therefore experience fewer nearest-neighbor electrostatic interactions than ions and water molecules within the cluster interior.

In our view, the observed variances of the dielectric storage and loss factors, ϵ' and ϵ'', respectively, and conductivity over the frequency range at a given temperature are largely governed (a) at low electrolyte concentrations simply by an increasing number of ionic charges (assumed mostly dissociated) per unit volume and (b) at high electrolyte concentrations by a decrease in the mobility of these charges due to their progressive association in pairs, then triplets, quartets, etc., with increasing concentration within the cluster "microsolutions".

The ϵ'' versus ω spectra for membranes incorporating all of each of the electrolytes we have used are clearly dominated by dc conduction. Long-range ion motions are manifest on log ϵ'' versus log ω plots by a rather linearly decreasing segment at low frequencies as illustrated in the example of Figure 1, which is that of membranes containing Zn^{2+} and SO_4^{2-} ions at various concentrations at 36 °C.[3] We had earlier considered this dc contribution to be a somewhat uninteresting and bothersome obscuration that required routine mathematical subtraction from the spectra to uncover hidden relaxation peaks.

In our previous reports we had argued that the high-frequency relaxation peaks extracted in this way were generated by the diffusion-controlled accumulation and dissipation of net ionic charge at the hydrophilic/hydrophobic phase boundaries along the direction of the applied electric field during a half-cycle of oscillation, during which time the field is unidirectional. As a perturbation, it is reasonable to expect that the oscillations of a single 40-Å scale macrodipole are electrically coupled to the oscillations of other cluster dipoles in the array, in particular to those adjacent to it. However, aside from such perturbations, this observed relaxation is considered to be a manifestation of the cooperative motions of hydrated ions on an *intracluster level.*

We have come to think of dc conduction within the context of these electrolyte-imbibed ionomers as involving

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