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A Novel Monomer and Polymers Based on 2,3,6,7-Anthracenetetracarboxylic Acid

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ABSTRACT: Novel poly(amic esters) and their corresponding polyimides containing the 2,3,6,7-anthracenetetracarboxy group were synthesized. Diester diacid chlorides were reacted with 4-aminophenyl ether in *N*-methyl-2-pyrrolidinone. A simplified method for the synthesis of an anti diester diacid chloride was developed. Intrinsic viscosities ranged from 1.44 to 0.20, dependent on anthracene-derived monomer content. Imidization of the poly(amic esters) takes place thermally in the range of 275−305 °C and was verified with IR. Thermogravimetric analysis indicates that the copolymers are more thermally stable than their pyromellitic acid-based counterparts. These materials have thermogravimetric temperatures in excess of 400 °C and degrade at greater than 580 °C. The polymers are fluorescent, but as a result of steric factors do not form an exciplex.

Anthracene-containing polymers are well-known in the open literature.[1] The polymer systems are diverse, but the polymers are based on a limited monomer set. Polymers containing anthracene show some of the chemical and physical properties of anthracene such as fluorescence[2] and the tendency of the anthracene nucleus to undergo 4 + 2 cycloaddition reactions across the 9,10 positions of the anthracene ring.[3] The peculiar polymerization of 9-vinylanthracene has been the subject of a review article.[4] Anthracene-containing polymers have been shown to form charge-transfer complexes with electron acceptors,[5] leading to the potential for new high-strength materials. Studies of anthracene-containing polymers have contributed to a greater understanding of physical macromolecular chemistry. Polarized fluorescence of anthracene nuclei incorporated by either 9,10 enchainment or by pendant substitution provides a very sensitive probe of macromolecular diffusion.[6] The phenomenon of spinodal decomposition was studied by the photochemical 4 + 4 cycloaddition of anthracene pendant styrene-based polymers.[7] Examples of polymers incorporating anthracene in the backbone have been shown to exhibit interesting photophysical characteristics and allowed photochemical cross-linking.[8]

To date, we are unable to locate examples in the open literature of polymers containing the 2,3,6,7-tetrasubstitution pattern. Most likely this is because the synthetic methodology required to assemble such molecules was underdeveloped. Earlier, Marshalk synthesized 2,3,6,7-anthracenetetracarboxylic acid in a five-step oxidation of 2,3,6,7-tetramethylanthracene to 2,3,6,7-anthracenetetracarboxylic acid.[9] Another three-step method based upon a benzo[1,2-*c*:4,5-*c*′]difuran intermediate has been used with success.[10,11] Recently we have reported an inexpensive one-step synthesis of compounds based on 2,3,6,7-anthracenetetracarboxylic acid in good yield.[12] Expanding this synthesis, we have developed a reactive monomer and polymers based on the 2,3,6,7-anthracenetetracarboxyl group. We report the successful synthesis of the reactive monomer, 2,6-(7)-bis[(*n*-butyloxy)carbonyl]-3,7(6)-anthracenedicarboxyl dichloride, as well as homo- and copoly(amic esters) and their corresponding polyimides with 4-aminophenyl ether and 2,5-bis[(cyclohexyloxy)carbonyl]-1,4-benzenedicarboxyl dichloride.

Experimental Section

Monomer Synthesis. Dichloromethane, triethylamine, and ethyl acetate were dried by distillation from calcium hydride. *N*-Methyl-2-pyrrolidinone (NMP) was distilled from phosphorus pentoxide. 4-Aminophenyl ether and pyromellitic anhydride were sublimed in vacuo. Dimethyl sulfoxide (DMSO) was Mallinkrodt spectral grade. All other solvents and reagents were purchased from Aldrich Chemical Co. and were used without further purification. NMR spectra were taken on Bruker AC series machines of the specified field. FAB mass spectra were taken on a Finnigan TSQ-70 mass spectrometer. FT/IR spectra were taken on a Perkin-Elmer 1760 X spectrometer.

2,3,6,7-Anthracenetetracarboxylic 2,3:6,7-Dianhydride (2). Finely ground 2,3,6,7-anthracenetetracarboxylic acid[12] (1.0 g, 0.002 83 mol) was dissolved in a mixture of 1.95 mL (1.42 g, 0.0141 mol) of dry triethylamine and 100 mL of dry dichloromethane, and the solution was treated with 0.627 mL (1.04 g, 0.008 46 mol) of acetyl bromide. A green precipitate formed immediately. The reaction was allowed to stir for 15 min. The resulting precipitate was filtered, washed with dichloromethane, and dried in vacuo. The yield of dianhydride was 0.72 g (79%): mp >300 °C dec in air, IR (KBr) 3446.3, 3036.6, 1838.1, 1792.6, 1724.4, 1238.9, 912.7 cm^{-1}.

2,6(7)-Bis[(*n*-butyloxy)carbonyl]-3,7(6)-anthracenedicarboxylic Acid (3). Dianhydride **2** (1.0 g, 0.003 14 mol) was warmed with 25 mL of dry *n*-butyl alcohol to 90 °C until a homogeneous solution was obtained (≈1.5 h). The excess *n*-butyl alcohol was removed from the filtered solution under reduced pressure, and the residue was chromatographed on silica gel (ethyl acetate/THF, 1:1). The product obtained, 1.12 g (76%), is a mixture of the syn and anti isomers: ^{1}H NMR (200 MHz, acetone-d_6) δ 8.98 (t, 2H), 8.67 (d, 2H), 8.50 (d, 2H), 4.33 (t, 4H), 1.75 (m, 4H), 1.47 (m, 4H), 0.96 (t, 6H); ^{13}C NMR (400 MHz, THF-d_8) δ 168.21, 168.03, 133.23, 133.04, 133.00, 132.80, 132.14, 132.06, 131.84, 131.73, 130.90, 130.82, 130.44, 130.33, 130.02, 129.64, 65.77, 31.58, 20.11, 14.12; IR (KBr) 3447.4, 2970.6, 2879.7, 2645.1, 1714.1, 1630.8, 1479.4, 1275.1, 1131.2, 934.4 cm^{-1}; MS *m*/*z* 466 (M^+).

2,6(7)-Bis[(*n*-butyloxy)carbonyl]-3,7(6)-bis(chlorocarbonyl)anthracene (4). Diester diacid **3** (4.10 g, 0.008 80 mol) was suspended in 50 mL of dry ethyl acetate. Oxalyl chloride (1.8 mL, 2.619 g, 0.0206 mol) was added, and the mixture was warmed to 40 °C; dissolution of the product was accompanied by evolution of gases. When gas evolution ceased, the ethyl acetate was stripped in vacuo and the residue recrystallized from cyclohexane, to which 2 drops of oxalyl chloride was added. The product was recovered by centrifugation and dried in vacuo; 3.81 g (86%) of a yellow solid was obtained; ^{1}H NMR

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Table 1. Properties of Copolymers

copolym composn calcd (% anthracene)	yield (%)	copolym composn by NMR (% anthracene)	intrinsic viscosity (dL/g)	temp at max rate of imidization (°C)	temp at max rate of decomposn (°C)
0.00	98	0.00	1.44	274	597
10.00	98	0.14	0.94	274	598
20.00	97	0.20	0.74	272	603
30.00	97	0.30	0.60	269	593
40.00	96	0.38	0.30	271	603
50.00	96	0.48	0.24	264	596
60.00	96	0.56	0.20	277	603
70.00	97	0.64	0.20	277	609
80.00	97	0.78	0.18	279	610
90.00	98	0.85	0.20	279	612
100.00	96	1.00	0.20	304	619

(200 MHz, $CDCl_3$) δ 8.71 (t, 2H), 8.57 (d, 2H), 8.55 (d, 2H), 4.27 (t, 4H), 1.80 (m, 4H), 1.50 (m, 4H), 1.00 (t, 6H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 167.4, 165.9, 133.9, 132.5, 132.3, 131.9, 131.8, 130.9, 130.5, 130.1, 128.1, 127.9, 66.4, 30.5, 19.2, 13.7.

1,4-Bis(chlorocarbonyl)-2,5-bis[(cyclohexyloxy)carbonyl]benzene (5). Pyromellitic dianhydride (10 g, 0.046 mol) was dissolved in 50 mL of dry cyclohexanol by heating the mixture to 90 °C until dissolved (≈1.5 h). The residual alcohol was evaporated in vacuo and the remaining viscous liquor triturated with hexane. A white amorphous solid was recovered; chromatography of 2.00 g of the material on silica gel (methyl acetate) afforded 1.42 g of the syn and anti diester diacid mixture: ^{1}H NMR (200 MHz, acetone-d_6) δ 8.24 (s, 1H), 8.08 (s, 2H), 7.95 (s, 1H), 5.00 (m, 2H), 1.98–1.33 (m, 20H). The diester diacid was converted to the diacid chloride by suspending 1.00 g (0.002 39 mol) in 25 mL of ethyl acetate and adding 0.500 mL (0.740 g, 0.005 83 mol) of oxalyl chloride and 1 drop of NMP. The mixture was stirred at room temperature until the suspension was totally dissolved and gas evolution had ceased. After evaporation of the solvent, the residue was recrystallized three times from dry hexane; 0.390 g of pure anti isomer was obtained: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.13 (s, 2H), 5.07 (m, 2H), 2.02–1.27 (m, 20H).

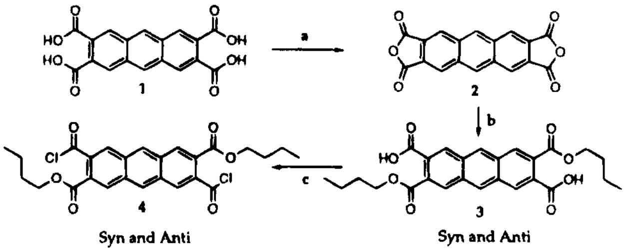
Polymer Synthesis. Steady-state fluorescence measurements were acquired with a Perkin-Elmer LS50 spectrofluorimeter. The solutions were excited at 380 nm with excitation and emission slit widths of 15 and 5 nm, respectively. After reprecipitation of polymers from NMP into deoxygenated water, the copolymer samples were dried in a vacuum oven at 120 °C overnight. Thermogravimetric measurements were carried out on a Seiko TG/DTA 220 instrument at a heating rate of 10 °C/min. A Seiko DSC 220C instrument in the oscillating mode was used for calorimetric determinations. The experiment was carried out under the following conditions: time–temperature wave frequency 0.01 Hz, temperature wave amplitude 4 °C, heating rate 2 °C/min, and data collection rate 2/s. Films for dynamic mechanical testing were cast from a 15% solution of the copolymer in DMSO into a glass plate and then dried under vacuum at 120 °C overnight. Dynamic mechanical tests were conducted on a Seiko DMS 200 spectrometer using a film measuring 20 × 5.0 × .022 mm at a frequency of 1 Hz and a heating rate of 2 °C/min.

Synthesis of Poly(amic esters). Poly(amic esters) were prepared according to the general method of Volksen et al.[13] The monomer stoichiometry was based upon a constant concentration of 4-aminophenyl ether (0.300 g, 0.0165 mol); the requisite molar ratio of diester diacid chlorides totaled 0.0165 mol. The diester acid chlorides were dissolved in 2 mL of THF and added to a stirred solution of the diamine in 2 mL of NMP. All operations were conducted in an inert atmosphere. The polymerization was allowed to proceed for 16 h before the polymer was isolated by pouring the reaction mixture into 250 mL of deoxygenated water. The compositions, yields, and intrinsic viscosities of the products are summarized in Table 1.

Discussion

The synthesis of the monomer from 2,3,6,7-anthracenetetracarboxylic acid is illustrated in Scheme 1. The anhydride is produced by an indirect route because 2,3,6,7-anthracenetetracarboxylic 2,3:6,7-dianhydride could not be obtained in satisfactory yield by sublimation. An attempt at sublimation caused an unacceptable decomposition of the product even at pressures of 10 mTorr. The insolubility of the tetraacid prevented its conversion to the dianhydride by refluxing in sodium acetate/acetic anhydride. As the tetraacid is soluble in a solution of triethylamine in dichloromethane, the best route to the dianhydride is through formation of a mixed anhydride with acetyl bromide. The mixed anhydride decomposes into acetic acid and the cyclic anhydride. When both rings are formed on the dianhydride, the resulting 2,3,6,7-anthracenetetracarboxylic 2,3:6,7-dianhydride precipitates from solution and is easily isolated by filtration.

Scheme 1. Synthesis of 2,6(7)-Bis[(*n*-butyloxy)carbonyl]-3,7(6)-anthracenedicarboxylic Dichloride



a: CH_2Cl_2 / $N(CH_2CH_3)_3$ CH_3COBr
b: n-Butanol / Δ
c: ClCOOCCl / $CH_3COOCH_2CH_3$

In addition to the anhydride bands at 1838 and 1793 cm^{-1}, the IR spectrum gives a carboxylic acid band at 1724 cm^{-1} which indicates that the dianhydride is not pure. 2,3,6,7-Anthracenetetracarboxylic 2,3:6,7-dianhydride is most soluble in hexamethylphosphoramide and slightly soluble in dimethyl sulfoxide. Recrystallization from these highly hygroscopic solvents is difficult and impractical. Attempts to sublime this material also fail due to excessive decomposition. The dianhydride readily reacts with *n*-butyl alcohol to give the corresponding syn and anti[14] di-*n*-butyl esters which are soluble in common solvents such as tetrahydrofuran.

This solubility of the diesters allows facile purification by column chromatography using 1:1 tetrahydrofuran/ethyl acetate as eluent. This method fails to separate the syn and anti isomers of the product as seen by the proton NMR. The apparent triplet at 8.79 ppm is comprised of two singlets corresponding to the unequivalent protons in the 9,10 positions of the syn diester and a central singlet corresponding to the equivalent protons in the 9,10 positions of the anti diester.

The reactive monomer is then formed cleanly by suspending the purified diesters in ethyl acetate and warming with oxalyl chloride. The resulting diester

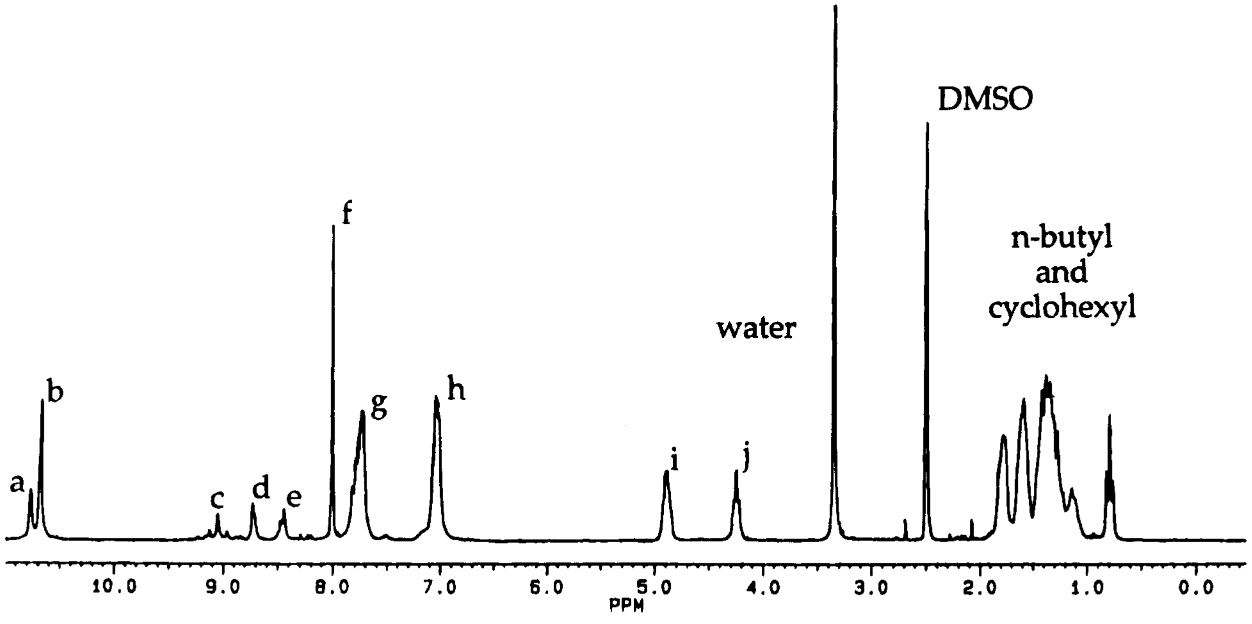
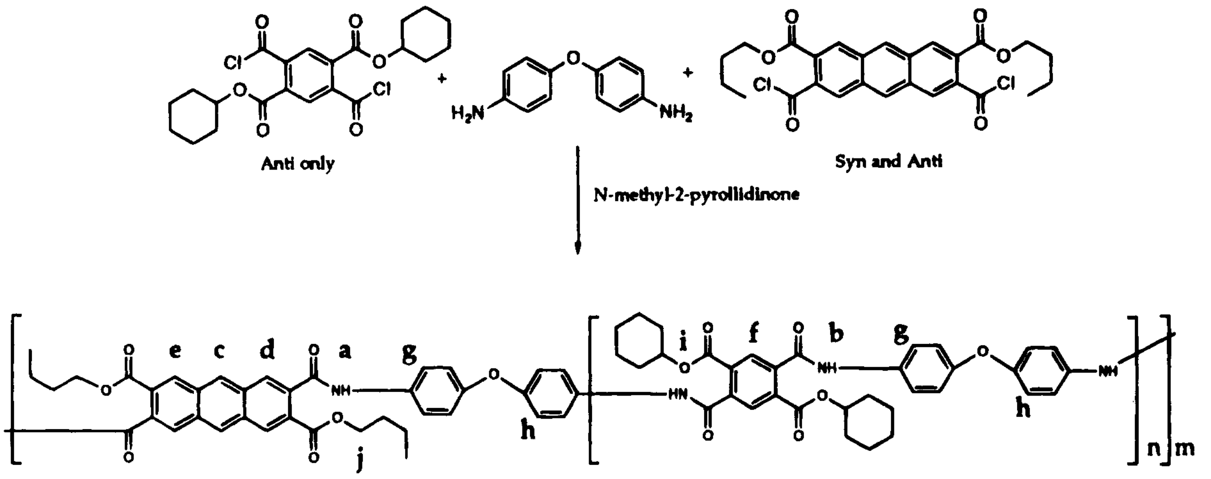


Figure 1. NMR spectrum of the 30% copolymer.

Scheme 2. Synthesis of Copolymers



diacid chloride is then recrystallized from cyclohexane. The recrystallization does not affect the separation of the syn and anti isomers of the diester diacid chlorides. By NMR the syn to anti isomer ratio of the diester diacid chloride matches that of the starting diester diacid at approximately 50:50.

An analogous monomer system, 2,5-bis[(cyclohexyloxy)carbonyl]-1,4-benzenedicarbonyl dichloride, was prepared in a manner similar to that of the anthracene-based monomer. The diester diacid was synthesized by heating pyromellitic dianhydride with excess dry cyclohexanol. The diesters were purified on a column using methyl acetate as the eluent and reacted with oxalyl chloride. The resultant mixture is then recrystallized from hexanes. Only the anti isomer recrystallizes as needles, while the syn isomer remains in solution. This is an improvement in the synthesis of anti diester diacid chlorides. When other analogs are used, such as the ethyl ester, a series of as many as 8–10 triturations with ethyl acetate are required to separate the syn and anti isomers of the diester diacid.[15] The corresponding anti diester diacid chloride is then prepared from the separated diester diacid.

The synthesis of the polymer systems is illustrated in Scheme 2. The intrinsic viscosity of the copolymer systems ranged from 1.44 dL/g in the case of the most rigid polymer based on the pyromellitic acid derived system. The intrinsic viscosity drops monotonically with the addition of the anthracene-derived monomer until its concentration reaches approximately 50%. From 50% anthracene monomer to the anthracene homopolymer, the intrinsic viscosity remains fairly constant at about 0.22 dL/g.

Figure 1 is the NMR spectrum of the 30% anthracene copolymer and its corresponding proton assignments. The anthracenic amide protons "a" resonate further downfield than those of the benzene-derived unit at "b" which is attributable to the anthracene ring's greater tendency to withdraw electrons. Proton signals "c" correspond to the protons in the 9,10 positions of the anthracene nucleus and show that the syn to anti diester distribution of anthracene units in the polymer is approximately 50:50. By comparing the integrals of the signals "i" and "j" corresponding to protons on the carbon adjacent to the oxygen in the esters, one may obtain the ratio of anthracene-derived units to benzene-derived units. This method allowed us to verify the composition of the copolymers.

As expected, all homo- and copoly(amic esters) in this series imidize thermally. The starting poly(amic esters)

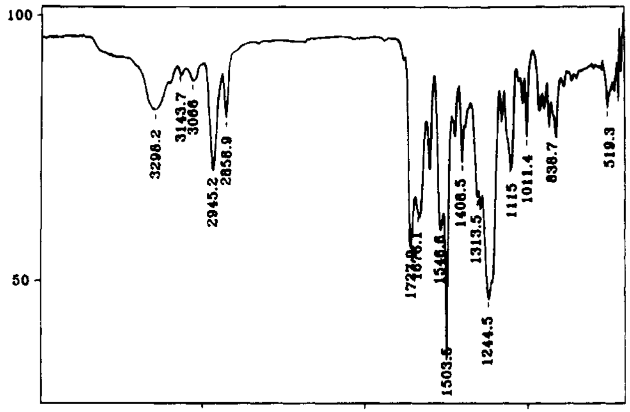


Figure 2. IR spectrum of 30% anthracene copoly(amic ester).

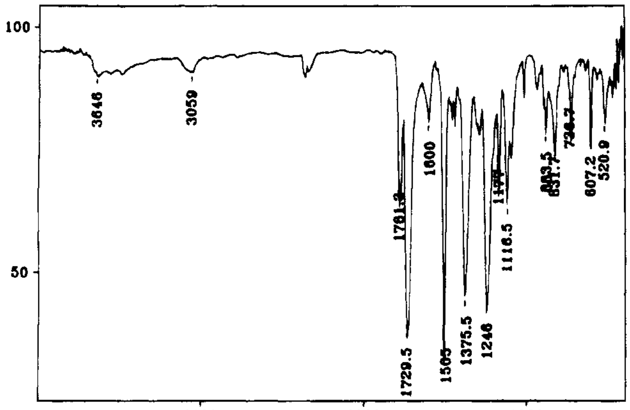


Figure 3. IR spectrum of imidized 30% anthracene copolymer.

are colorless to lemon yellow in color depending upon anthracene-derived monomer content, while the resultant polyimides are red–brown in color and take a darker brown color with increasing anthracene-derived monomer content. A very thin film of 30% anthracene-derived polymer was cast on a NaCl plate, and its IR spectrum is given in Figure 2. Evident in this spectrum are the N–H stretching band at 3298 cm^{-1}, the C–H stretching bands at 2945 and 2859 cm^{-1}, and the amide and ester carbonyl stretching bands between 1676 and 1728 cm^{-1}. The sample was then baked at 320 °C for 4 h under nitrogen to give an imidized film whose IR spectrum is given in Figure 3.

The transition to the imidized polymer is quite pronounced. In addition to a shifting of the carbonyl stretching frequencies, the bands corresponding to N–H stretching of the amide functions as well as the C–H stretching bands corresponding to the aliphatic ester groups have vanished. Furthermore, the heat-treated film shows the four bands characteristic of imide structures.[16] The symmetric and asymmetric carbonyl stretches occur at 1781 and 1730 cm^{-1}, respectively. The other associated bands are the C–N stretch at 1376 cm^{-1} and the band at 737 cm^{-1} which is deformation of the imide ring to imide carbonyls. The IR spectrum of all the copolymers was nearly identical regardless of anthracene monomer content.

Thermal Analysis

A representative TG/DTG analysis of the 30% anthracene copolymer is shown in Figure 4. The thermogram shows two major features. The first is due to the imidization of the poly(amic ester) with concomitant loss of *n*-butyl and cyclohexyl alcohol. The 27.7% loss of mass corresponds almost exactly to the calculated value of 27.5% for the requisite elimination of alcohols. The resultant polyimide is stable up to about 550 °C. The maximum rate of decomposition of the anthracene-containing homopolyimide is in excess of 615 °C/min.

Table 1 includes TG/DTA data for the copolymer series. In general, the onset of imidization takes place at between 200 and 250 °C. Imidization requires progressively higher temperatures as the copolymers become richer in anthracene-derived units. This is not surprising since a study of the thermal imidization of methyl-, ethyl-, *n*-propyl-, and *n*-butylpoly(amic esters) showed that the rate of imidization for the butyl ester was as much as 60 times slower than that for the other esters.[17] After imidization, the trend is toward an incremental increase in thermal stability of the polyimides with increasing concentrations of anthracene-containing monomer in the polymer. This increase in thermal stability for this series of polymers appears to be linear, but the data are slightly scattered due to a statistically insufficient number of samples from different synthetic runs.

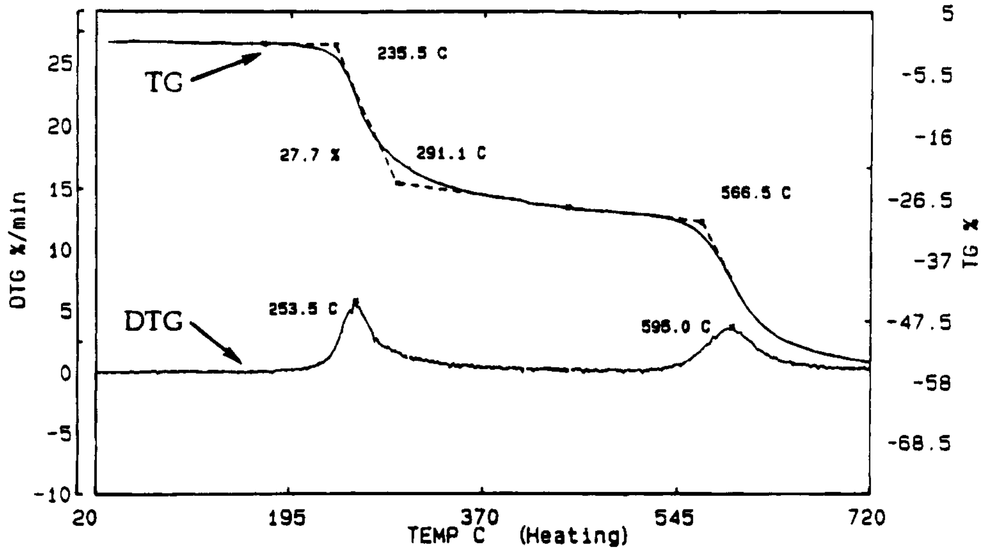


Figure 4. TG/DTA data from the 30% anthracene copolymer.

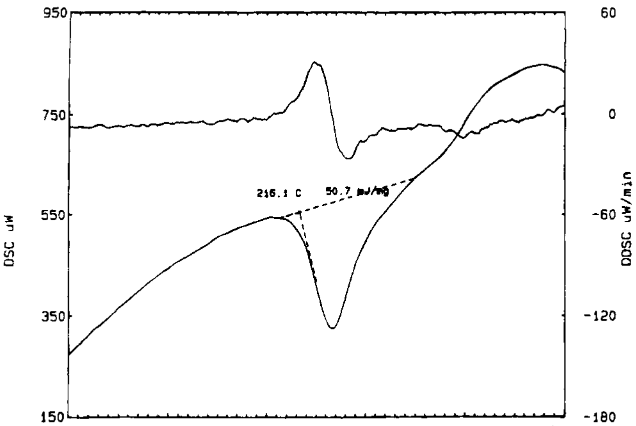


Figure 5. Oscillation mode DSC of 30% copolymer; 1st heating.

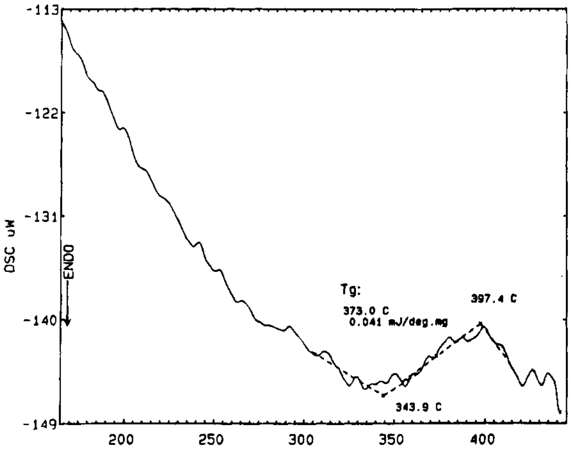


Figure 6. Oscillation mode DSC of 30% copolymer; 2nd heating.

Calorimetric studies on the 30% anthracene copoly(amic ester) were performed by DSC in the "modulated" or "oscillation mode".[18] Separation of the convoluted scan yields a "thermal" or "reversible" component and a "kinetic" or "irreversible" component. The thermal component of the first heating is indicated in Figure 5. The endotherm between 215 and 280 °C corresponds to imidization. An integration of the signal within this endothermic peak gives the heat of imidization for this copolymer of approximately 50.7 J/g.

After cooling the sample below the imidization temperature, it was subjected to a second heating. The kinetic component of this signal is shown in Figure 6. This analysis shows a weak glass transition temperature, T_g, at approximately 397.4 °C and the absence of any other significant thermal transition in this temperature range.

Both the imidization and the glass transitions of these materials are well illustrated in the dynamic mechanical analysis of the 30% copoly(amic ester) film (Figure 7). We may think of Young's modulus of elasticity, E, as being the sum of two components, E' and iE'', relating to the elastic and viscous properties of a given material, respectively. A dynamic mechanical glass transition occurs when the imaginary component, E'', known as the loss modulus, reaches a maximum, while the real component, or storage modulus, E', reaches a minimum. A composite term called tan δ, is the ratio of E''/E'. The term relates to an angle, δ, describing the phase lag in the elastic response of a sample due to its viscous nature. In region 1 of Figure 7, a dynamic mechanical glass transition of the poly(amic ester) occurs at approximately 230 °C. This transition was not observed in the modulated DSC experiment. In region 2, a peak in tan δ corresponding to the imidization reaction occurs at about 240 °C. Also, there is a corresponding increase in the storage modulus. In region 3 a dynamic mechanical glass transition temperature of the polyimide appears at approximately 414 °C. The dynamic mechanical measurement corresponds within 25 °C to the modulated DSC measurement for the glass transition temperature of the polyimide. The results of this mechanical test will not give correct values for the Young's moduli as the cross section of the film shrank considerably during the test.

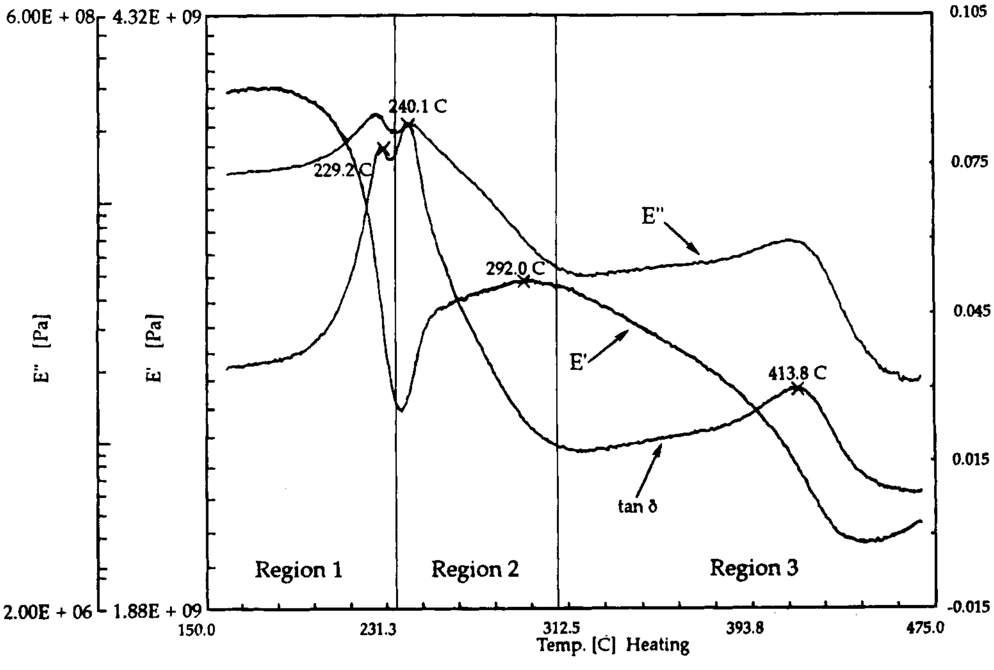


Figure 7. Dynamic mechanical test of 30% copolymer.

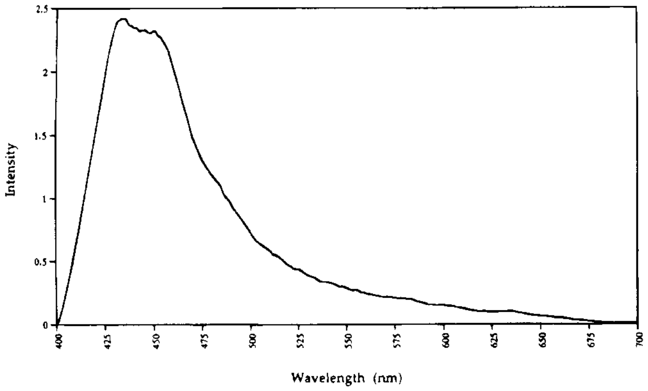


Figure 8. Fluorescence of the 30% copoly(amic ester).

Fluorescence

In addition to being more thermally stable than their pyromellitic acid based counterparts, the anthracene moiety imparts a tendency of these polymers to fluoresce both in the solid state and in solution. We have investigated the fluorescence of these materials in solution. Figure 8 is the fluorescence spectrum of the 30% copoly(amic ester) in DMSO at a concentration of 0.004 33 g/dL (2.20 × 10^{-5} M in chromophore). The excitation spectrum consisted of a broad featureless hump with a maximum at about 386 nm. We chose 380 nm as the excitation wavelength.

Care must be taken in such measurements, however, as it is known that anthracene-containing polymers have been shown to form interchain photodimers when exposed to ultraviolet radiation.[19] At least five fluorescence scans were taken per sample, and no decrease in fluorescence intensity was observed. Since formation of the 4 + 4 photodimer entails loss of the fluorophore, this possibility was discounted.

The first band associated with anthracene occurs at approximately 425 nm. This is significantly red shifted from that of pure anthracene, which occurs at 380 nm. This can be attributed to the lowering of energy of the S^0 to S^1 transition due to the increase in conjugation associated with the carbonyl groups on the anthracene nucleus. UV absorption spectra were taken in DMSO and showed that the homopolymer containing no anthracene moieties started absorbing at around 380 nm and the absorbance increased exponentially going toward lower wavelengths. Therefore, the pyromellitic acid derived repeat units could not absorb fluorescence light from the anthracene fluorophore. This implies that there will be no energy transfer from anthracene-based units to non-anthracene-based units in the chain.

A series of solutions of our copoly(amic esters) were prepared such that the chromophore concentration remained constant at 2.20 × 10^{-5} M. The fluorescence intensity as well as the spectral shape remained the same regardless of the percentage of anthracene monomer in the copolymer. These spectra are quite different from that of poly[2-(9-anthryl)ethyl methacrylate].[20] None of our poly(amic esters) show the broad band between 430 and 670 nm characteristic of exciplex formation, the intensity of which is an indicator of chromophoric interaction during the excited-state lifetime.[21] Poly[2-(9-anthryl)ethyl methacrylate] is a flexible backbone polymer with pendant anthryl units. The mobility of the chain as well as the mobility of the pendant chromophores allows efficient interaction among chromophores. Since the chromophores in our polymers are incorporated along their long axis in the backbone of the polymer, their mobility is diminished compared to poly[2-(9-anthryl)ethyl methacrylate]. The geometry of the anthracenetetracarboxyl site is also deleterious to the formation of an exciplex. To understand the local environment of the anthracene moiety, the compound 2,6-bis[(*n*-butyloxy)carbonyl]-3,7-anthracenedicarboxylic bis(4-oxyphenyl)phenyldiamide was modeled using SYBYL[22] on a VaxStation 2300. The minimization was conducted using Hückel parameters for the calculations of electrostatics. The result of the calculation in the form of a space-filling model is presented in Figure 9. Two major factors influence the steric environment around the anthracene moiety. The first is the bending of the ester carbonyl away from the plane of the anthracene ring. The second and more influential steric effect is that of the amide's phenyl ring being rotated out of the plane of the anthracene ring. In order for the formation of an exciplex to occur, molecules must achieve parallel alignment with spacing within 5–6 Å. 2,3,6,7-Anthracenetetracarboxyl-containing poly(amic esters) are not able to form exciplexes due to unfavorable steric interference of the ester and amide groups.

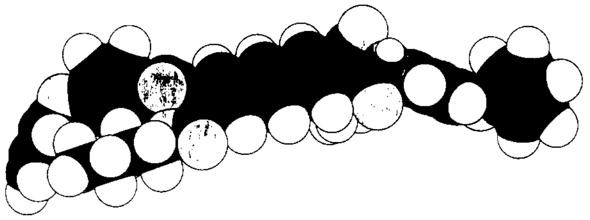


Figure 9. Space-filling model of the anthracene fragment.

Conclusion

We have prepared the first soluble poly(amic esters) and high-temperature polyimide polymers based on 2,3,6,7-anthracenetetracarboxylic acid. Polymers containing this unit are fluorescent. We have shown that copolyimides containing both 2,3,6,7-anthracenetetracarboxyl and 1,2,4,5-benzenetetracarboxyl units are high-temperature materials exhibiting a tendency toward higher thermal stability with increasing concentrations of anthracene-containing units in the polymer. Copoly(amic esters) containing anthracene-derived monomers have a glass transition of greater than 400 °C and decompose at greater than 580 °C.

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(14) In most of the literature concerning poly(amic esters) to date, diacid chloride diesters based on pyromellitic acid are called "ortho" or "meta" isomers. While this is sufficient for pyromellitic acid based compounds, it is not for fused linear aromatic acids such as 2,3,6,7-naphthalene- or 2,3,6,7-anthracenetetracarboxylic acids. We therefore recommend "syn" and "anti" as the more appropriate nomenclature. In the case of other tetracarboxylic acids, such as 3,3′,4,4′-biphenyltetracarboxylic acid, the diesters are most appropriately described using IUPAC nomenclature.

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