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Synthesis and properties of aromatic polyamides and polyesters containing spiroacetal and silphenylene units

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Summary

New polyamides and polyesters containing spiroacetal and silphenylene units were prepared by the low-temperature interfacial polycondensation reaction of 4,4'-diaminodibenzalpentaerythritol (4-ABP) or 4,4'-dihydroxydibenzalpentaerythritol (4-HBP) with bis(4-chlorocarbonylphenyl)dimethylsilane (DMS) or bis(4-chlorocarbonylphenyl)diphenylsilane(DPS). The resulting polymers have inherent viscosities in the range of 0.13~0.90 dL/g at 30℃ in *N,N*-dimethylacetamide. These polymers were readily soluble in various polar solvents and were able to be cast into transparent and tough films. The glass transition temperatures of the polymers were detected in the range of 161~253℃ in their differential scanning calorimetry traces. No evidence of melting point was observed in all polymers. The solution-casted film of polyamide (PA-I) derived from 4-ABP and DMS showed ultimate strength of 73.4 MPa and initial modulus of 13.4 GPa.

Introduction

Polymers having spiroacetal units exhibit excellent transparency, good mechanical properties, good hardness, heat and water resistance, and low birefringence (1-6). For this reason, this class of polymers is considered to be multi-functional, and it is useful as heat-resistant materials, curing agents for epoxy resins after functionalization, photomemory disks, etc. Furthermore, polyspiroacetals composed of rod-like chain structures may be considered to be high performance fibers on the condition that they can be made more processable. Double strand polyspiroacetals or polymers which have their spiroacetal moieties connected directly to phenylene groups, however, have not been able to be processed for practical use because of their insolubility and infusibility resulting from polymer backbone stiffness.

One of attempts to increase processability is the introduction of hetero atoms along the polymer backbone. In our earlier papers, it was reported that polyamides containing silicon atoms dissolved in various organic solvents without losing their intrinsic thermal stability (7,8). In this paper we report the synthesis, characterization and preliminary properties of aromatic polyamides and polyesters containing both spiroacetal and silphenylene moieties in their polymer backbone.

Experimental Part

Materials

p-Toluenesulfonic acid (Aldrich) was purified according to the method described in the literature (9). Dowex 50W-X16 ion exchange resin (Dow Chemical) was dried by reflux for 24 hrs in 30% sulfuric acid. *N,N*-dimethylacetamide (Aldrich) and benzene (Merck) were dried over calcium sulfate and calcium chloride, respectively, and subsequently distilled before use. Pentaerythritol (Aldrich), p-nitrobenzaldehyde (Aldrich) and p-hydroxybenzaldehyde (Aldrich) were used as received.

Measurements

IR spectra were obtained using a Bio-Rad FT-IR spectrophotometer. A Bruker 300MHz ^{1}H-NMR spectrometer was employed for the polymer structure analyses. Elemental analyses were carried by a Perkin-Elmer Model-240 C/H/N Analyzer. A differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA) (DuPont 9900) were used for the study of thermal behavior and stability of polymers. Wide angle X-ray patterns were recorded using nickel-filtered CuKα(λ=1.540Å) radiation on a Rigaku Geiger Flex D-Max X-ray diffractometer. Inherent visco- sities of the polymers were measured at a concentration of 0.5 g/dL in *N,N*-dimethylacetamide at 30℃. The evaluation of ultimate strength and initial modulus of polyamide film was performed with a Ultem Instron 4206.

Monomer Synthesis

Bis(4-chlorocarbonylphenyl)dimethylsilane (DMS) and bis(4-chlorocarbonylphenyl)diphenylsilane (DPS) were synthesized by chlorination and oxidation after Grignard reaction of dimethyldichlorosilane or diphenyldichlorosilane with p-tolylmagnesium bromide as reported in the literature (10,11).

4,4'-Dinitrodibenzalpentaerythritol (4-NBP): A mixture of 0.5 g of p-toluenesulfonic acid, 6.8 g of pentaerythritol, and 15.12 g of p-nitrobenzaldehyde in 100 mL of benzene was refluxed for 5hrs. After the condensed water was collected in a Dean-Stark trap, the reaction mixture was evaporated to dryness. The crude product was washed with hot water several times, recrystallized from ethylene glycol diacetate, and dried in a vacuum oven. Yield 72%. m.p. 234-235℃. IR (KBr, cm^{-1}): ν=2800-3000 (CH), 1610, 1520 (Ar C=C), 1520, 1340 (NO_2), 1470-1490 (-CH_2-), 1410 (tert. -CH); 1240, 1200, 1110, 1070, 1020 (spiro C-O). ^{1}H-NMR (DMSO-d_6, ppm): δ=3.7-4.9 (m, 8H, -CH_2-), 5.7 (s, 2H, spiro CH), 7.7 (m, 8H, Ar-H). Anal. Calcd for $C_{19}H_{18}N_2O_8$ (402.36): C, 56.72; H, 4.51; N, 6.96. Found: C, 56.87; H, 4.62; N, 6.98.

4,4'-Diaminodibenzalpentaerythritol (4-ABP): A mixture of 10.27 g of 4-NBP and 0.5 g of 10% palladium on carbon in 150 mL of dimethylformamide was stirred at room temperature under hydrogen at ordinary pressure until the theoretical amount of hydrogen was consumed. The solution was filtered, and filtrate was poured into large volume of cold water. The precipitate was collected, purified by recrystallization from alcohol, and dried under vacuum. The yield was 71% (6.11 g). m.p. 165-169℃. IR (KBr, cm^{-1}): ν=3320, 3410 (NH_2), 1470, 1490 ($-CH_2-$), 1410 (tert. CH), 1220, 1175, 1155, 1110, 1070, 1050 (spiroacetal C-O), 1610, 1520 (Ar C=C), ^{1}H-NMR (DMF-d_7, ppm): δ=3.4-4.7 (m, 8H, $-CH_2-$), 5.2 (s, 4H, NH_2), 5.4 (s, 2H, spiro -CH-), 6.4-7.2 (m, 8H, Ar-H). Anal. Calcd for $C_{19}H_{22}N_2O_4$ (342.39): C, 66.65; H, 6.48; N, 8.18. Found: C, 66.88; H, 6.65; N, 8.36.

4,4'-Dihydroxydibenzalpentaerythritol (4-HBP): A mixture with 48 g of dried Dowex 50W-X16 resin, 266 g of DMSO and 330 g of benzene was refluxed at 92-94℃ for 12 hrs. After removing the water which was collected in a Dean-Stark trap, 50 g of pentaerythritol and 91.6 g of 4-hydroxybenzaldehyde were added to the above mixture and refluxed at the same temperature for an additional 24 hrs. The Dowex resin was filtered off, and the residue (filtrant) was slowly poured into benzene, while stirring constantly. The precipitated products were separated by filtration, washed with benzene several times, and dried under vacuum. Yield 71%. m.p. 245-255℃. IR (KBr, cm^{-1}): ν=3325 (OH), 1490-1470 ($-CH_2-$), 1410 (C-H), 1220, 1175, 1155, 1110, 1070, 1050 (spiroacetal C-O). ^{1}H-NMR ($CDCl_3$, ppm): δ=3.5-4.0 (m, 8H, $-CH_2-$), 4.6-4.8 (d, 2H, =CH-), 5.47 (s, 2H, -OH), 6.7-6.9 (m, 4H, aryl CH *ortho to* OH), 7.2-7.4 (m, 4H, aryl CH *ortho to* OH). Anal. Calcd for $C_{19}H_{20}O_6$ (344.36): C, 66.27; H, 5.85. Found: C, 66.32; H, 5.69.

Polymerization

All the polymers were prepared by low temperature interfacial polycondensation method. A typical polymerization method is described below.

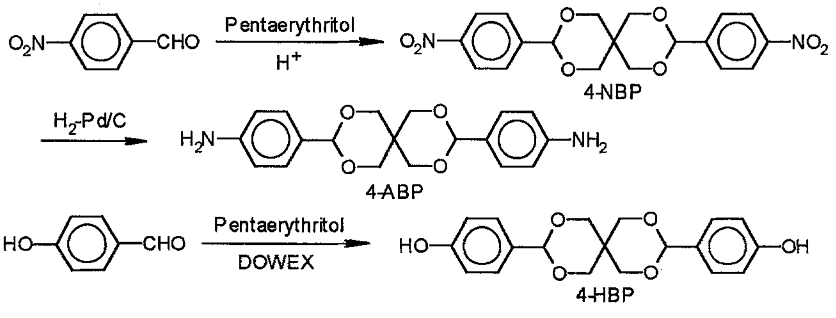
Synthesis of polyamide (PA-I): In a reactor equipped with mechanical stirrer were placed 3.42 g (0.01mol) of 4-ABP and 1.06 g of sodium carbonate in 75 mL of water at 0℃. To this was added 3.38 g (0.01mol) of DMS in 120 mL of methylene chloride at the same temperature, and the mixture was stirred for 30 min. The contents were poured into a large volume of methanol. The polymer was separated by filtration, and washed successively with water, acetone and methylene chloride. The polymer was purified by dissolving in dimethylacetamide, filtering the solution and pouring the filtrate into a large volume of water. The resultant polymer was filtered, washed with acetone and dried under vacuum at 100℃ for 24 hrs. The yield was 77%. Polyamide, PA-II, was prepared in a similar manner.

Synthesis of polyester (PES-I): In a reactor equipped with mechanical stirrer were placed 3.44 g of 4-HBP and 0.8g of sodium hydroxide in 75 mL of water at 0℃. To this was added 3.71 g of DMS in 100 mL of methylene chloride at the same temperature and the mixture was stirred for 3 hrs. The contents were poured into a large volume of methanol. The polymer was separated by filtration, and washed with water and methanol. The polymer was purified by dissolving in N,N-dimethylacetamide, filtering the solution and pouring the filtrate into a large volume of water. The resultant polymer was filtered, washed with acetone and dried under vacuum at 100℃ for 24 hrs. The yield was 82%. The polyester, PES-II, was prepared in a similar manner.

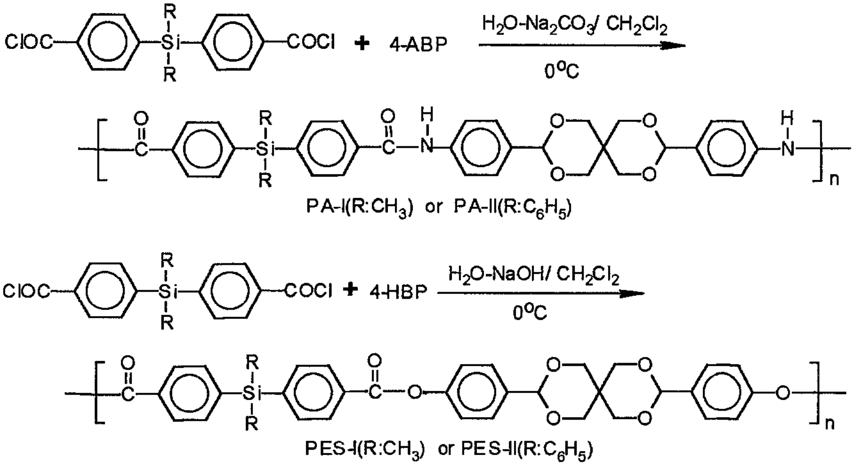
Results and discussion

The spiroacetal-containing diamine and diol were synthesized starting from p-hydroxybenzaldehyde or p-nitrobenzaldehyde with pentaerythritol as shown in Scheme 1. The silicon-containing acid chlorides, DMS and DPS, were prepared as reported in the literature (10,11). From these monomers, two polymer series, i.e., spiroacetal-containing polyamides and polyesters having silphenylene units in their polymer backbone were obtained by low temperature interfacial polymerization method in alkaline conditions. The polymerization proceeds as depicted in Scheme 2. The structures of the resulting polymers were identified by IR and ^{1}H-NMR spectroscopy. As a representative, IR spectrum of polyamide

Scheme 1:



Scheme 2:



PA-I showed characteristic absorption bands at 3290 cm^{-1} (N-H), 1600 cm^{-1} (amide C=O), 1220-1050 cm^{-1} (spiroacetal C-O), and 840 and 800 cm^{-1} (Si-CH_3). The peaks which appeared at 3.6-4.9 ppm in the ^{1}H-NMR spectra were attributed to the spiroacetal ring protons. Silyl methyl protons exhibited signal at 0.6 ppm and aromatic protons showed signals at 7.3-8.3 ppm (Figure 1). The structures of polyesters were also confirmed by IR and ^{1}H-NMR spectroscopy.

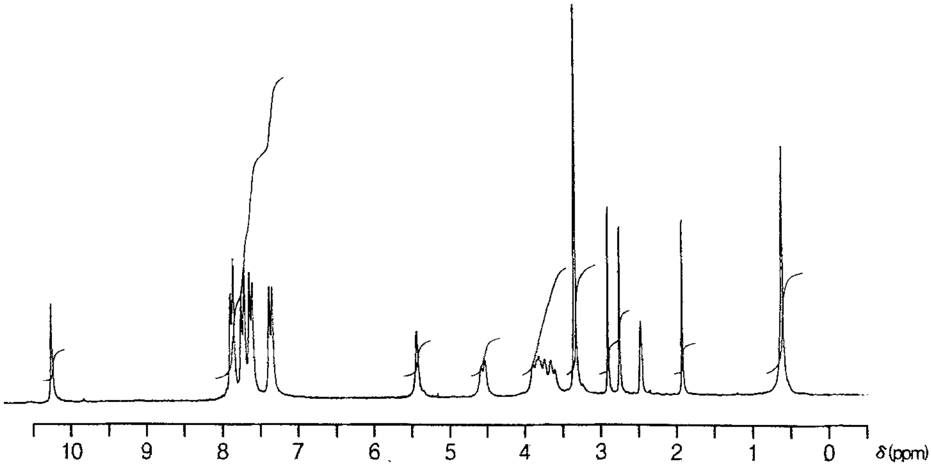


Figure 1. ^{1}H-NMR spectrum of PA-I (DMSO-d_6)

The polymerization conditions, elemental analysis data, yields, and inherent viscosities of PA-I, PA-II, PES-I and PES-II are listed in Table 1. Satisfactory C/H ratios by elemental analysis were obtained for all

Table 1. Reaction Conditions, Yields, Inherent Viscosities and Elemental Data of Spiroacetal Containing Polymers

Polymer	Reaction temp (℃)	Reaction time (h)	Yield (%)	IV[a] (dL/g)	C(%)		H(%)		N(%)	
					Cal.	Found	Cal.	Found	Cal.	Found
PA-1	0	0.5	77	0.90	69.28	68.88	5.65	5.63	4.62	4.60
PA-II	0	0.5	74	0.70	73.95	73.02	5.24	5.20	3.83	3.82
PES-I	0	0.5	82	0.13	69.06	68.55	5.30	5.15	-	-
	0	3	80	0.49	69.06	68.92	5.30	5.21	-	-
PES-II	0	0.5	84	0.20	73.75	73.16	4.96	4.87	-	-
	0	3	78	0.49	73.75	73.51	4.96	4.88	-	-

a : Measured at a concentration of 0.5g/dL in N,N-dimethylacetamide at 30℃.

polymers. The polymer yields were 74-84% after purification. On examining the inherent viscosities of polymers, it was found that the molecular weights are much dependent on the reactivity of the spiroacetal-containing monomer's functional group. Compared to the polyesters derived from 4-HBP, the polyamides obtained from 4-ABP showed high viscosities. This suggests that spiroacetal-containing diamine monomer is relatively more reactive than the corresponding diol monomer under similar condition.

It is known that wholly aromatic polyspiroacetals are insoluble in common organic solvents. However, the polymers having silicon units are soluble in polar solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulphoxide and N-methylpyrrolidone. This enhanced solubility indicates that the introduction of silicon atoms in rigid polymer backbone can affect the chain stiffness to be reduced.

The thermal properties of the polyamides and polyesters were evaluated by DSC and TGA. The results are tabulated in Table 2. All of the samples did not show any melting points besides the glass transition at 161-253℃ by DSC traces. This means that the silicon-containing polymers are non-crystalline. The amorphous nature of these polymers could be also proved by wide angle X-ray scattering. Polymer PA-II has the highest glass transition temperature among the present polymers, probably due to more aromaticity and hydrogen bonding of amide linkage. Figure 2 illustrates the TGA curves for PA-I, PA-II, PES-I and PES-II. All the polymers showed similar decomposition patterns, and no weight losses were observed below 275℃. The TG curves revealed initial decomposition at 275-306℃ and 10% weight loss at 365-423℃ under nitrogen atmosphere. The polymers changed the color from yellow to brown around decomposition temperatures.

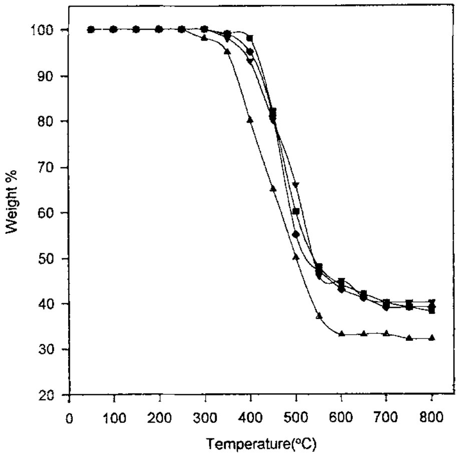


Figure 2. TGA curves of prepared polymers(20℃/min in N_2); PA-I(◆), PA-II(■), PES-I(▲), and PES-II(▼).

Table 2. Thermal properties of polyamides and polyesters

Polymer	T_g[a] (℃)	T_0[b] (℃)	T_{10}[c] (℃)	Char yield at 800℃ (%)
PA-I	240	303	420	39
PA-II	253	306	423	38
PES-I	161	275	365	32
PES-II	203	302	410	40

a: Glass transition temperature.
b: Initial decomposition temperature.
c: Temperature of 10% weight loss.

For the purpose of measuring mechanical properties, the polymer film of PA-I was prepared by casting the 20% solution in *N,N*-dimethylacetamide onto a glass plate. To ensure complete removal of the solvent, the film was heated overnight at 110℃ and for 5 hrs at 150℃ in a vacuum oven. The ultimate strength and initial modulus of that polymer film were 73.4 MPa and 13.4 GPa, respectively. The comparison of the value for commercialized poly(butylene terephthalate) or poly (ethylene terephthalate) with PA-I's indicated that the spiroacetal-containing silicon polyamide has a good mechanical properties. Thus, these series of polymers will have potential usefulness for high performance engineering plastics.

Conclusion

The new spiroacetal and silphenylene-containing polymers were successfully synthesized by the low-temperature interfacial polymerization of 4-ABP or 4-HBP with DMS or DPS as comonomers. The introduction of silphenylene units into the rigid polyspiroacetal backbone caused soluble aromatic polyspiroacetal with good thermal stability. Thus, the resulting polyamides and polyesters are considered as new promising processable high temperature polymeric materials.

Acknowledgement

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