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New Poly[bis(benzimidazobenzisoquinolinones)]

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ABSTRACT: A series of new poly[bis(benzimidazobenzisoquinolinones)] has been obtained by the condensation of 4,4′-oxydinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (**1a**), 4,4′-(phenylene-1,3-dioxy)dinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (**1b**), 4,4′-(sulfonylbis(*p*-phenyleneoxy))dinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (**1c**), and 4,4′-(isopropylidenebis(*p*-phenyleneoxy))dinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (**1d**) with aromatic tetraamines. The polycondensations were carried out at high temperature in *m*-cresol containing benzoic acid. The polymers are soluble in *m*-cresol and phenol–chlorinated hydrocarbon mixtures. Tough, flexible films can be cast from dilute solutions. The polymers are amorphous and show good thermal and oxidative stability.

Introduction

Poly[bis(benzimidazobenzophenanthrolines)] belong to a group of ladder heterocyclic polymers exhibiting high thermal stability and good chemical resistance. The first polymers of this type were obtained by Van Deusen[1-3] from the polycondensation of 1,8:4,5-naphthalenetetracarboxylic dianhydride with aromatic tetraamines. These polymers showed high softening temperatures and were soluble only in strong acids (polyphosphoric acid, concentrated H_2SO_4, and methanesulfonic acid), which severely restricted their applications. Subsequent investigations on the chemical modification of poly[bis(benzimidazobenzophenanthrolines)] involved the insertion of dioxyarylene, dioxydiarylene,[4] or hexafluoropropylidene[5] linkages between the rigid aromatic–heterocyclic condensed units of the polymer chain. As a result, polymers soluble in organic solvents (*m*-cresol and phenol–chlorinated hydrocarbon mixtures) with glass transition temperatures below their respective decomposition temperatures were obtained. The flexible linkages were introduced into the polymer chain by the use of suitable tetraamine monomers. However, the methods of preparing such monomers are very cumbersome and expensive, which severely restricts the applications of these polymers.

The aim of our investigations was the preparation of fusible and soluble poly[bis(benzimidazobenzisoquinolinones)], which also belong to the poly[bis(benzimidazobenzophenanthroline)] class of ladder polymers. The monomers selected for their preparation were commercial aromatic tetraamines and dinaphthalene-derived dianhydrides, obtained from acenaphthene.

Experimental Section

Monomers. 3,3′-Diaminobenzidine (2a). This commercially available reactant was purified by recrystallization from deoxygenated water under an inert atmosphere, mp 177–179 °C (lit.[6] mp 178–179 °C).

3,3′,4,4′-Tetraaminodiphenyl ether (2b) was obtained by the procedure described in ref 7, mp 150–151 °C (lit.[8] mp 149–151 °C).

Bis(3,4-diaminophenyl)methane (2c) was prepared as previously described,[8] mp 139–140 °C (lit.[8] mp 137–138 °C).

4,4′-Oxydinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (1a) was prepared from acenaphthene according to the scheme given in ref 9. A solution of 4.3 g (0.025 mol) of 5-hydroxyacenaphthene, obtained as described in ref 10–12, and 0.1 g (0.0005 mol) of *p*-toluenesulfonic acid in 13 mL of 1,2,4-trichlorobenzene was heated for 35 h at 185 °C in an inert atmosphere. The solvent was removed by distillation. The residue was dissolved in 150 mL of benzene and extracted with 1 N NaOH to remove unreacted 5-hydroxyacenaphthene. After evaporation of the solvent, the crude product was purified by chromatography on silica gel (Kieselgel 100, 70–230 mesh) with a 9:1 hexane–benzene mixture as the eluent, yielding 2.3 g (56.7%) of white crystalline 5,5′-oxydiacenaphthene (mp 149 °C): IR (Nujol) $\nu_{C\text{-}O\text{-}C}$ 1250, $\nu_{C=C}$ 1590 cm^{-1}; molecular mass in mass spectrum, *m/e* 322. Anal. Calcd for $C_{24}H_{18}O$ (322.43) C, 89.4; H, 5.6. Found: C, 89.2; H, 5.3.

A solution of 2.0 g (0.006 mol) of 5,5′-oxydiacenaphthene and 16.4 g (0.06 mol) of sodium dichromate in 150 mL of glacial acetic acid was refluxed for 6 h. The reaction mixture was then poured into 200 mL of water. The precipitate that formed was collected by filtration and dissolved in 500 mL of 20% Na_2CO_3. The solution was filtered and acidified to afford a crude product. Crystallization from dimethylformamide (DMF) yielded 1.6 g (63%) of the yellowish final product **1a**: mp 356 °C dec; IR (Nujol) $\nu_{C=O}$ 1730, 1770, $\nu_{C\text{-}O\text{-}C}$ 1250, $\nu_{C=C}$ 1595 cm^{-1}; molecular mass in mass spectrum, *m/e* 410. Anal. Calcd for $C_{24}H_{10}O_7$ (410.36): C, 70.2; H, 2.5. Found: C, 69.9; H, 2.3.

4,4′-(Phenylene-1,3-dioxy)dinaphthalene-1,8:1′,8′-tetracarboxylic dianhydride (1b) was prepared by the published procedure [13] with several modifications. To a stirred solution of 29.09 g (0.105 mol) of 4-bromo-1,8-naphthalic anhydride in 250 mL of dimethylformamide under nitrogen at 70 °C was added 7.70 g (0.05 mol) of the disodium salt of resorcinol over 0.5 h. The mixture was heated to 140 °C and maintained at that temperature for 8 h. After cooling, the solution was poured into water (~500

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mL) to precipitate the crude product. It was filtered, washed with water, and dried at 100 °C. Recrystallization from DMF and extraction with a 1:2 Ac_2O-AcOH mixture afforded 18.0 g (71.7%) of the dianhydride as a pale yellow solid: mp 310–311 °C (lit.[13] mp 271–272 °C); IR (KBr) $\nu_{C=O}$ 1770, 1735 cm^{-1}; molecular mass in mass spectrum, *m/e* 502. Anal. Calcd for $C_{30}H_{14}O_8$ (502.44): C, 71.71; H, 2.80. Found: C, 72.02; H, 2.60.

4,4′-(Sulfonylbis(*p*-phenyleneoxy))dinaphthalene-1,8:1′,8′-tetracarboxylic Dianhydride (1c). A solution of 8.3 g (0.003 mol) of 4-bromo-1,8-naphthalic anhydride in 150 mL of *N*,*N*-dimethylacetamide (DMAA) was added dropwise under a nitrogen atmosphere to 4.1 g (0.0015 mol) of the disodium salt of 4,4′-dihydroxydiphenyl sulfone. The resulting slurry was vigorously stirred, heated to 140–150 °C, and maintained at that temperature for 8 h. The reaction mixture was cooled to room temperature and poured into 400 mL of a 1:1 ethanol-water mixture. The yellow solid that formed was collected by filtration, dried at 150 °C, and recrystallized from DMAA to yield 7.8 g of **1c** (81%): mp >360 °C (lit.[13] mp >400 °C); IR (KBr) $\nu_{C=O}$ 1770, 1730 cm^{-1}; molecular mass in mass spectrum, *m/e* 642. Anal. Calcd for $C_{36}H_{18}O_{10}S$ (642.59): C, 67.28; H, 2.82. Found: C, 66.98; H, 2.59.

4,4′-(Isopropylidenebis(*p*-phenyleneoxy))dinaphthalene-1,8:1′,8′-tetracarboxylic Dianhydride (1d). The synthesis of **1d** using 4-bromo-1,8-naphthalic anhydride and the disodium salt of 2,2-bis(4-hydroxyphenyl)propane was carried out by a procedure identical with that described for **1c**; yield 70%, mp 294–295 °C; IR (KBr) $\nu_{C=O}$ 1770, 1730, ν_{CH_3} 2980, δ_{CH_3} 1380, 1365 cm^{-1}; ^1H NMR (DMF) τ 8.14 (6 H, s, CH_3), 2.58–2.78 (8 H, m, Ar), 1.0–2.4 (10 H, m, Ar); MS, *m/e* 606 (M^+–CH_3), 620 (99.1%), 502 (29.7%), 409 (11.7%). Anal. Calcd for $C_{39}H_{24}O_8$ (620.61): C, 75.48; H, 3.90. Found: C, 75.30; H, 3.80.

Polycondensation Reactions. The general procedure for the polycondensation reaction was as follows: Equimolar amounts of each monomer (1.75 mmol of the dianhydride and 1.75 mmol of the tetraamine) and 2 mmol of benzoic acid were added to freshly distilled *m*-cresol heated at 70 °C under an inert atmosphere. The vigorously stirred mixture was heated gradually to 180 °C for 4 h and then maintained at that temperature for 4–7 h. After being cooled to room temperature, the solution was added dropwise to 50 mL of ethanol to precipitate nearly quantitative amounts of polymer (the polymers **3a** and **3b** precipitated during the reaction). The product was extracted overnight with ethanol and dried at 100 °C under reduced pressure.

All the polymers were heated under vacuum (1 h at 100 °C, 1 h at 200 °C, and 2 h at 250 °C) to effect complete cyclization. The cyclization process was followed by IR measurements. IR spectra of the polymers were compared with those of model compounds.

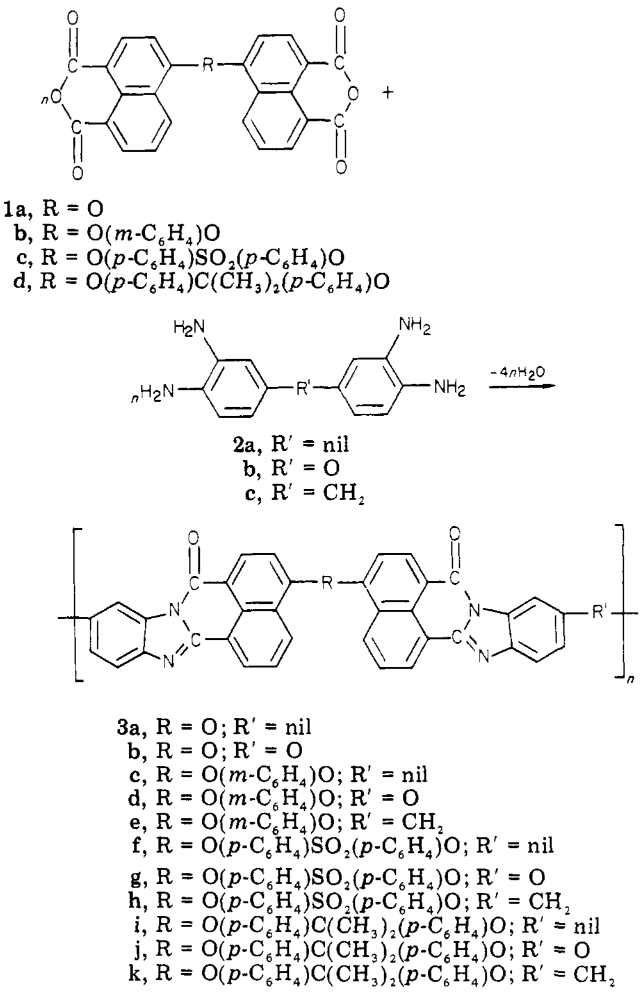
Model Compounds. *N*,*N*′-Diphenyl-4,4′-(isopropylidenebis(*p*-phenyleneoxy))dinaphthalene-1,8:1′,8′-tetracarboxylic Diimide (4). A vigorously stirred slurry of 1.86 g (3 mmol) of dianhydride **1d** and 0.75 g (8 mmol) of aniline in 10 mL of freshly distilled *m*-cresol was slowly heated to 190 °C (4 h) under an inert atmosphere and maintained at that temperature for 10 h. The solution was cooled to room temperature and poured into 50 mL of ethanol. The precipitate was collected by filtration and extracted with ethanol. Recrystallization from DMF afforded 1.9 g (85.2%) of a fine white crystalline product: mp 335–336 °C; IR (KBr) $\nu_{C=O}$ 1720, 1680 cm^{-1}. Anal. Calcd for $C_{51}H_{34}O_6N_2$: C, 79.46; H, 4.45; N, 3.63. Found: C, 79.43; H, 4.32; N, 2.92.

4,4′-(Isopropylidenebis(*p*-phenyleneoxy))bis(7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one) (5a–c). The synthesis of **5a–c** was conducted under the same conditions as outlined for the compound 4. Dianhydride **1d** (1.86 g, 3 mmol), *o*-aminoaniline (0.735 g, 6.8 mmol) and benzoic acid (0.55 g, 4.5 mmol) were used. Recrystallization from DMF afforded 1.8 g (78.6%) of yellow fine-crystalline product **5a–c**: mp 320–324 °C; IR (KBr) $\nu_{C=O}$ 1715, $\nu_{C=N}$ 1610, 1550 cm^{-1}. Anal. Calcd for $C_{51}H_{32}O_4N_4$: C, 80.08; H, 4.22; N, 7.33. Found: C, 79.86; H, 3.98; N, 6.47.

Results and Discussion

The new poly[bis(benzimidazobenzisoquinolinones)] were obtained by a one-step, high-temperature solution polycondensation, according to Scheme I.

Scheme I



1a, R = O
b, R = O(m-C_6H_4)O
c, R = O(p-C_6H_4)SO_2(p-C_6H_4)O
d, R = O(p-C_6H_4)C$(CH_3)_2$(p-C_6H_4)O

2a, R′ = nil
b, R′ = O
c, R′ = CH_2

3a, R = O; R′ = nil
b, R = O; R′ = O
c, R = O(m-C_6H_4)O; R′ = nil
d, R = O(m-C_6H_4)O; R′ = O
e, R = O(m-C_6H_4)O; R′ = CH_2
f, R = O(p-C_6H_4)SO_2(p-C_6H_4)O; R′ = nil
g, R = O(p-C_6H_4)SO_2(p-C_6H_4)O; R′ = O
h, R = O(p-C_6H_4)SO_2(p-C_6H_4)O; R′ = CH_2
i, R = O(p-C_6H_4)C$(CH_3)_2$(p-C_6H_4)O; R′ = nil
j, R = O(p-C_6H_4)C$(CH_3)_2$(p-C_6H_4)O; R′ = O
k, R = O(p-C_6H_4)C$(CH_3)_2$(p-C_6H_4)O; R′ = CH_2

The syntheses were carried out in *m*-cresol in the presence of benzoic acid, which acted as a catalyst. The IR spectra of the polymers were compared with those of the model compounds: bis(naphthalimide) 4 and the isomeric bis(benzimidazobenzisoquinolinones) **5a–c**. The model compounds were synthesized by the following reactions shown in Scheme II.

The IR spectra of the polymers resembled those of the model compound **5a–c**, especially in the wavenumber region of from 1750 to 1300 cm^{-1}.[14,15] Both in the IR spectra of the polymers studied and in the model compound **5a–c** absorption bands at 1715 cm^{-1} were observed along with weak IR absorption bands at 1610 and 1550 cm^{-1}, typical of the =C=N group vibrations. The former are known to be due to the characteristic stretching vibrations of the >C=O group in the pyridinone ring.

The IR spectra of the polymers investigated were also found to exhibit rather weak absorption bands, characteristic of the naphthalimide-type model compound 4 (1720 and 1680 cm^{-1}) and corresponding to the C=O stretching vibration in a six-membered imide ring. The above quoted absorption bands made possible the estimation of the degree of cyclization attained in the polymers synthesized. The one-stage polycondensation method was not found to yield completely cyclic structures, and therefore all polymers were subjected to additional annealing at 200–300 °C in vacuo, in order to achieve complete cyclization.

The IR spectra of the thus thermally treated polymer (polymer **3i**) are compared in Figure 1 with those of the monomer **1d** and the model compounds 4 and **5a–c**. It is apparent from the comparison of these spectra that a high degree of cyclization has been attained in the polymer **3i**.

Table I
Properties of Poly[bis(benzimidazobenzisoquinolinones)] 3 Obtained from Dianhydrides 1a-d and Tetraamines 2a-c[a]

polymer 3	η_{red},[b] dL/g	T_d, °C		solubility[d]				T_g, °C
		argon	air	conc H_2SO_4	CF_3COOH	*m*-cresol	3:1 $C_2H_2Cl_4$-PhOH	
a	0.98	510	490	s	s	i	i	$>T_d$
b	0.90	520	490	s	s	i	i	$>T_d$
c	1.10[c]	490	470	s	s	i	i	395
d	0.68	490	490	s	s	ss	ss	368
e	0.29	460	440	s	s	ss	ss	
f	0.49	450	430	s	s	s	s	404
g	0.30	460	430	s	s	s	s	360
h	0.20	450	430	s	s	s	s	380
i	1.00	460	450	s	s	s	s	373
j	0.75	460	450	s	s	s	s	312
k	0.37	460	440	s	s	s	s	355

[a] Monomer concentration 0.35 mol/L. [b] In a 3:1 tetrachloroethane-phenol mixture at 25 °C. [c] In concentrated H_2SO_4 at 25 °C. [d] s = soluble; ss = sparingly soluble, i = insoluble.

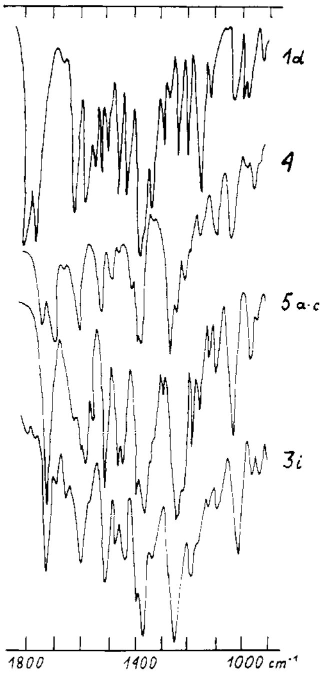


Figure 1. Infrared absorption spectra of the dianhydride **1d**, the model compounds **4** and **5a-c**, and the poly[bis(benzimidazobenzisoquinolinone)] **3i**.

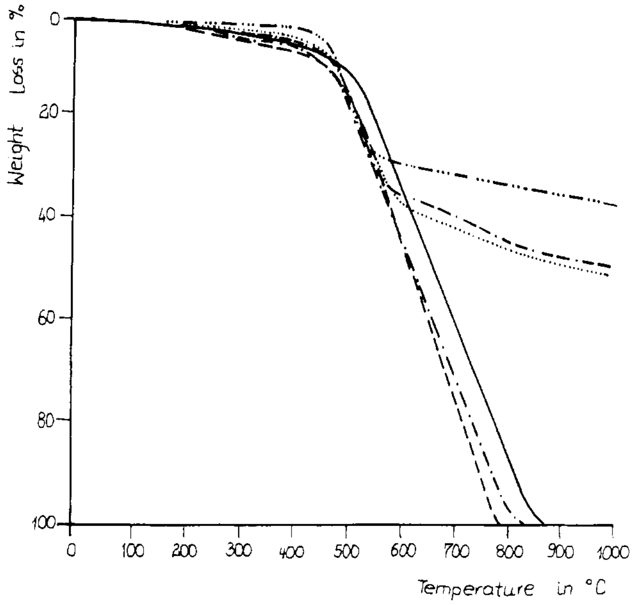


Figure 2. Thermogravimetric analyses of the polymers **3i-k** synthesized from the dianhydride **1d** and various tetraamines (heating rate 10 °C/min): (—) polymer **3i** in air; (---) polymer **3j** in air; (-·-) polymer **3k** in air; (·---·) polymer **3i** in argon; (···) polymer **3j** in argon; (-···-) polymer **3k** in argon.

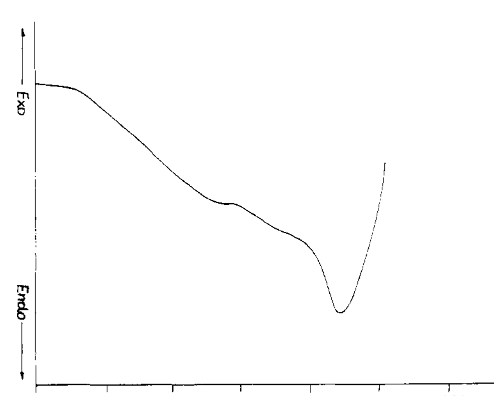
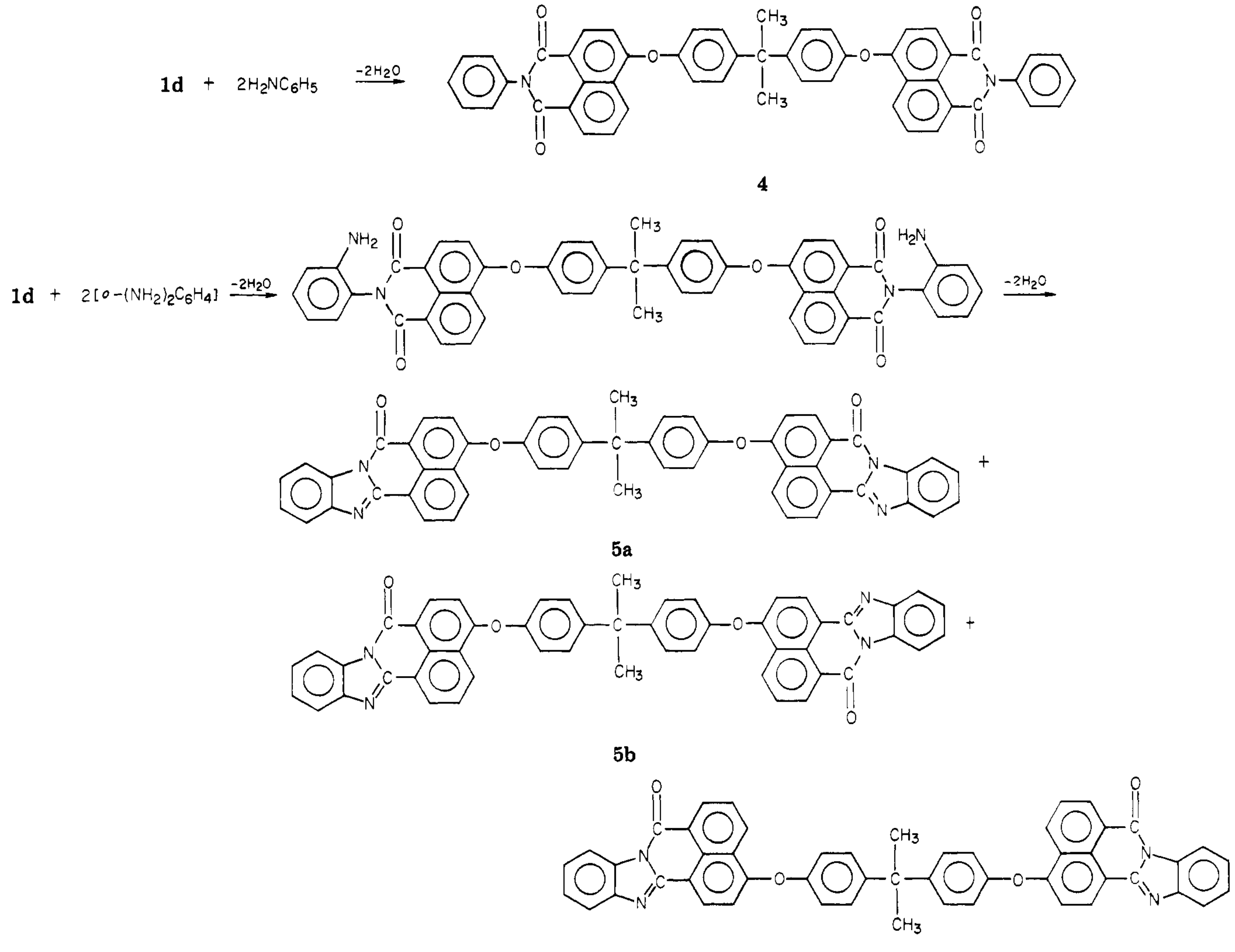


Figure 3. DSC curve of the polymer **3j** (DuPont Model 990 thermoanalyzer, heating rate 20 °C/min, nitrogen atmosphere).

Properties of the newly synthesized polymers are listed in Table I. The obtained polymers were found to be soluble in strong acids (concentrated H_2SO_4, methanesulfonic acid, polyphosphoric acid); some of them, particularly those containing 1,3-phenylenedioxy linkages and the O or CH_2 linkages (polymers **3d** and **3e**) were also found to be soluble in *m*-cresol and in a 3:1 mixture of tetrachloroethane-phenol. Tough, flexible films were obtained from 6% solutions in a 3:1 mixture of tetrachloroethane-phenol of the polymers **3i** and **3j** containing isopropylidenebis(*p*-phenyloxy) groups. The molecular weights and the solubilities of the remaining polymers were not sufficient for film formation.

Influence of the presence of various linkages making the poly[bis(benzimidazobenzisoquinolinone)] chain more flexible on the thermal stability of the polymers was also investigated. Results of thermogravimetric analyses are listed in Table I, typical thermogravimetric curves obtained for polymers synthesized from one of the dianhydrides (**1d**) and different tetraamines being shown in Figure 2. As expected, the poly[bis(benzimidazobenzisoquinolinones)] exhibited an outstanding thermal stability in an inert atmosphere and in air. Their temperatures at the beginning of decomposition, T_d, were greater than 430 °C in air and over 450 °C in argon, while weight loss at 800 °C amounted, on average, to some 25-50%. Thermal stability

Scheme II



4

5a

5b

5c

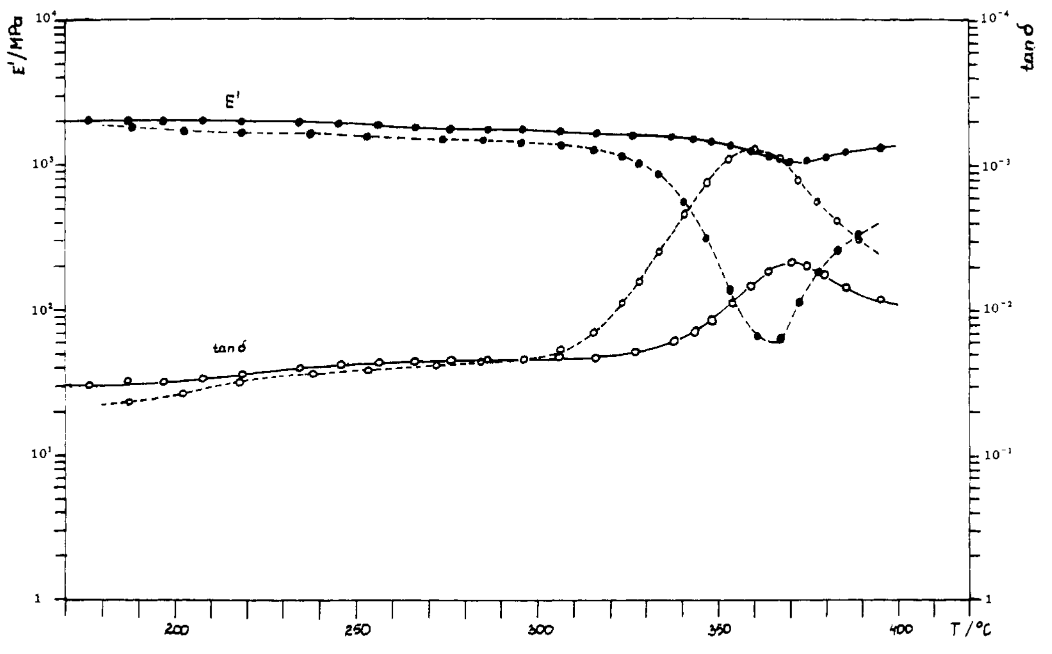


Figure 4. Storage modulus *E'* and loss tangent vs. temperature for the polymers **3i** (—) and **3j** (---) determined by using a Rheovibron viscoelastometer (frequency 3.5 Hz, heating rate 2 °C/min).

of these polymers was found to depend on the amount of flexible or kinked linkages per repeating unit of the chain. Polymers **3a** and **3b**, having one or two ether linkages in the repeating chain unit, exhibited the highest thermal stability. On the other hand, the introduction of further ether linkages and *m*-phenylene rings (polymers **3c** and

3d) was found to result in the reduction of the T_d by some 10–20 °C. A lowering of the T_d value was also observed to take place on the introduction of sulfone and methylene linkages (polymers **3f–k**).

On the basis of DSC measurements it was shown (Table I and Figure 3) that some of these new polymers had glass transition temperatures T_g below their decomposition temperatures, a distinct relationship being found to exist between the molecular structure of the polymers studied and their T_g values. An increase in the amount of linkages making the polymer chain more flexible was accompanied by a decrease of T_g. Consequently, except for the polymers **3a** and **3b**, containing from one to two flexible linkages per repeating chain unit, for the remaining polymers it was shown that $T_g < T_d$.

Thermomechanical analyses carried out for the polymers **3i** and **3j**, forming strong polymeric films with tensile strengths of the order of 1000 kG/cm^2 at 20 °C (elongation 7–12%), showed that the thus obtained T_g values were higher by some 10–20 °C than those determined by DSC measurements.

X-ray analysis results showed the polymers herein described to be amorphous.

Conclusions

The above presented poly[bis(benzimidazobenzisoquinolinones)] constitute a group of macromolecular compounds exhibiting novel properties, hitherto unreported for polymers of that class. And thus, in sharp contrast to the poly[bis(benzimidazobenzophenanthrolines)] based on the 1,4:5,8-naphthalenetetracarboxylic dianhydride,[2,3] these new polymers are soluble not only in strong acids but also in organic solvents and exhibit glass transition temperatures that are below their corresponding decomposition temperature values while preserving a relatively high thermal and oxidative stability.

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Telechelic Perfluorocarbons. α,ω-Perfluorodicarboxylic Acids

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ABSTRACT: A homologous series of α,ω-perfluorodicarboxylic acids is generated in a controlled free radical polymerization of tetrafluoroethylene using aqueous peroxydisulfate with either an iron or a copper promoter. Even-numbered C_4 to C_{16} perfluorodicarboxylic acids are the major species formed, although small, but discrete quantities of the odd-numbered C_3 to C_{15} analogues are detected. Some higher molecular weight carboxylated poly(tetrafluoroethylene) is also isolated. The mass spectral cracking pattern of the methyl esters shows an unusual "unzipping" of tetrafluoroethylene units, especially with the higher molecular weight oligomers. A mechanism for chain initiation and termination of perfluoroalkyl radicals leading to carboxylic acid end groups is discussed.

Introduction

Since poly(tetrafluoroethylene)[1] exhibits a number of useful chemical and physical properties, it would be desirable to construct oligomeric perfluoroalkyl units with functionality at both termini, i.e., telechelic perfluorocarbons,[2] as building blocks for other polymers. Indeed, examples are to be found in the extant literature in which perfluoroacyl fluorides have been selectively photocoupled to higher molecular weight diacyl fluorides,[4] and α,ω-diiodoperfluoroalkanes have been generated from the controlled reaction of tetrafluoroethylene with iodine.[5,6]

In this paper we present the free radical oligomerization of tetrafluoroethylene as a route to a homologous series of α,ω-perfluorodicarboxylic acids. Previous reports[7,8] on the reaction of tetrafluoroethylene with free radical initiators describe the formation of high molecular weight, insoluble polymers, showing some evidence of carboxylic acid functionality when aqueous peroxydisulfate was used as the initiator.[9] However, the more common synthetic routes to perfluorodicarboxylic acids involve the oxidative cleavage of carbon–carbon double bonds present in either perfluorocycloalkenes[10,11] or perfluoro-α,ω-diolefins.[12] We thought a method for the preparation of perfluorodicarboxylic acids directly from tetrafluoroethylene could be developed if the reaction were carried out in a controlled aqueous environment of free radicals derived from peroxydisulfate and metal ions, i.e.

$$(n/2 + 1)\mathrm{CF_2{=}CF_2} + \mathrm{S_2O_8}^{2-} \xrightarrow[\mathrm{H_2O}]{[\mathrm{M}^{n+}]} \mathrm{HO_2C(CF_2)_{\mathit{n}}CO_2H}\ \text{etc.} \quad (1)$$

Since such an oligomerization occurs perforce in competition with the ready polymerization of tetrafluoroethylene, we carried out all of our reactions at relatively low pressures of monomer and high concentrations of initiator. The dichotomy between oligomerization and polymeriza-