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Synthesis of novel silicon-modified polymides

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Summary

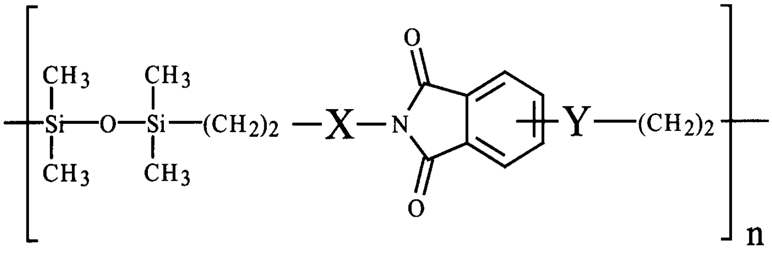
A series of new poly(siloxane imide)s from *N*,*N*-dialkenylimides and 1,1,3,3-tetramethyldisiloxane via polyhydrosilylation was synthesised. The polymer obtained from hydroquinone bis[(*N*-allylphthalimide)-4-carboxylate] showed liquid crystalline properties. Its mesophase was in the range of 107-197°C.

Introduction

Polyimides and copolyimides are known as materials of high temperature resistance and good transparency (1,2). Unfortunately, these polymers are extremely intractable, being insoluble in most organic solvents. Polyimides present processing problems and considerable effort is still being devoted to improve these properties. A number of methods have been used to overcome intractability while maintaining high thermal stability. These include incorporation to polymeric units flexible groups such as oxyethylene or methylene chains (3,4). Also, the use of monomers with heteroatoms in the main chain or with large pendant groups improves polymers' solubility and processing.

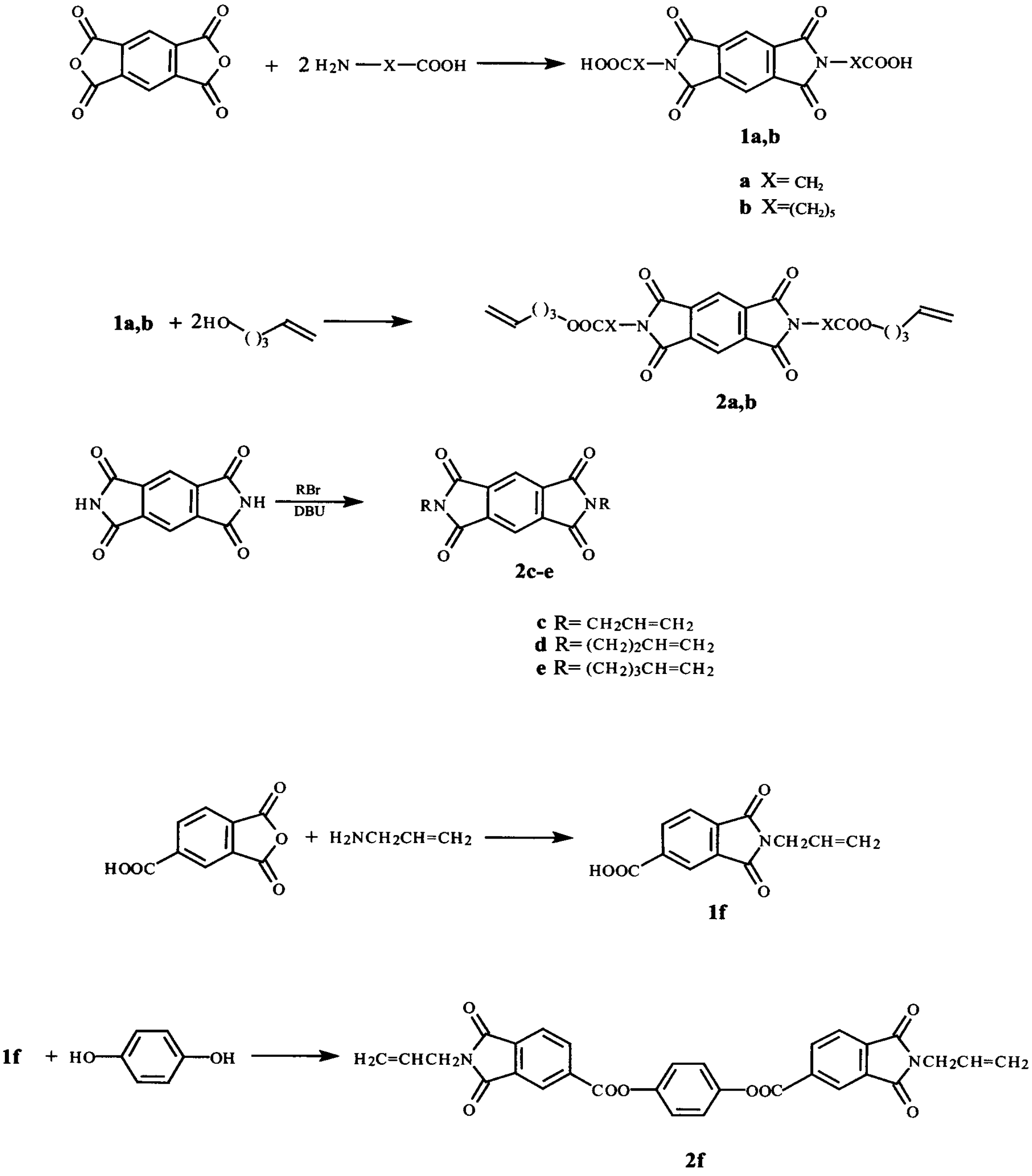
On the other hand silicon containing polymers are known as well soluble materials. They are also thermoplastic and exhibit good adhesion. The incorporation of flexible silicone moieties connecting the rigid imide units remarkably improves processability of polyimides.

Poly(siloxane imide)s, PSIs, are usually synthesised via a condensation of silicon containing monomers (1,5-7), i.e. diamines or dianhydrides. We suggest another possibility, typical for silicon containing polymers, the polyhydrosilylation reaction of an imide with two terminal alkene groups. The hydrosilylation reaction, i.e. the addition of a silane to an alkene, is an important reaction in organo-silicon chemistry (8). It may proceed thermally or in the presence of variety of catalysts e.g. hexachloroplatinic acid, dichloro(endo-dicyclopentadiene)platinum or platinum tetramethyl-divinyldisiloxane (PTDD) (9-12). In the present study we synthesised a series of new copolyimides of general formula given below carrying imide moieties and 1,1,3,3-tetramethyldisiloxane unit.



The pathways of these syntheses have been presented on the Schemes 1 and 2.

Experimental



Scheme 1

All chemicals used were analytical-grade commercial products and were used without any further purification.

Bis-(N-carboxymethylene)pyromellitimide ***1a:*** The imide was obtained according to the method described earlier from pyromellitic anhydride and aminoacetic acid. M.p. 344°C [m.p. lit.(13) 345°C].

Bis-[N-(6-carboxypentamethylene)]pyromellitimide 1b: The imide was obtained according to the similar method described earlier, m.p. 238°C [m.p. lit.(14) 234-6°C].

N-allyltrimellitimide ***1f:*** Stochiometric amounts (10 mmol) of allylamine and trimellitic anhydride were refluxed in DMF for 2 h. Then mixture was purred into diluted HCl. The crude product was crystallised from 70% ethanol; m.p. 155°C, [m.p. lit.(15) 159°C].

Bis(N-carboxymethylene)pyromellitimide dipentenoate ***(2a)*** *and bis[N-(6-carboxypentamethylene)]pyromellitimide dipentenoat**e (2b):*** Stochiometric amounts of **1a** or **1b** (10mmol) and 4-penten-1-ol (1.74g, 20mmol) were dissolved in 30cm^3 of CH_2Cl_2 and 5,15g (25mmol) of DCC (1,3-dicyclohexylcarbodiimide) was added. The mixture was stirred at room temperature for 6h. The crude product was isolated by standard procedure. A purification was performed by column chromatography (SiO_2) using $CHCl_3$/ethyl acetate (4:1) system as an eluent.

2a: Yield 2.1g (45%). m.p. 131-2°C. Elemental anal. ($C_{24}H_{24}N_2O_8$; 468.5): calc.: C 61.53, H 5.16, N 5.98, found: C 61.65, H 5.05, N 5.87. FTIR data (CH_2Cl_2, in cm^{-1}): 1778, 1742, 1721, 1520, 1492, 1389. ^{1}H NMR data ($CDCl_3$, in ppm): 1.75(m,4H,CH_2), 2.13(m,4H,CH_2), 4.19(t,4H,CH_2O), 4.50(s,4H,CH_2N), 5.02(m,4H,CH_2=), 5.77(m,2H,CH=), 8.37(s,2H,ArH).

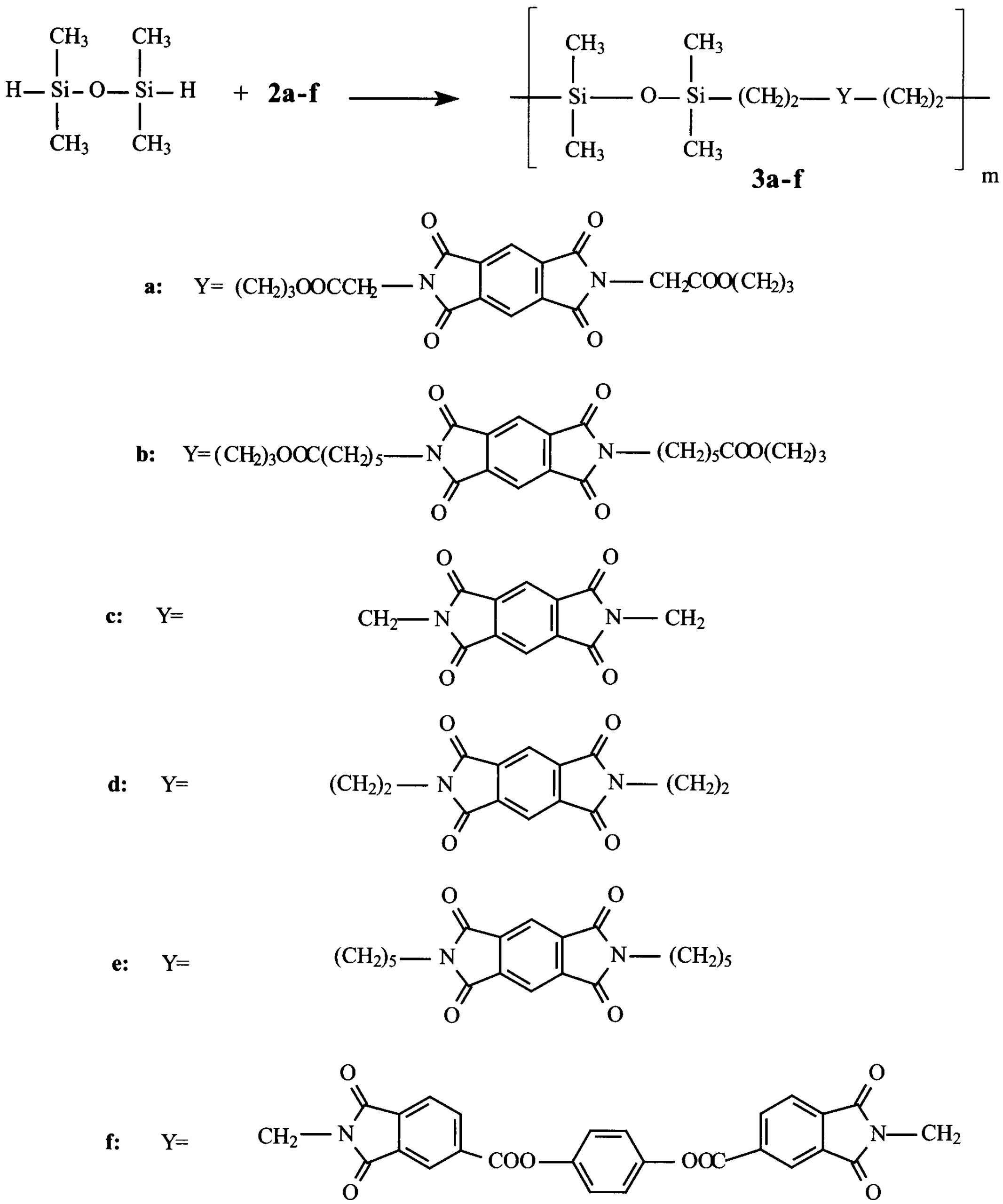
2b: Yield 1.9g (33%). m.p. 107-8°C. Elemental anal. ($C_{32}H_{40}N_2O_8$; 580.7): calc.: C 66.19, H 6.94, N 4.82, found: C 66.27, H 7.00, N 4.70. FTIR data (CH_2Cl_2, in cm^{-1}): 1776, 1744, 1720, 1521, 1489. ^{1}H NMR data ($CDCl_3$, in ppm): 1.40(m,4H,CH_2), 1.71(m,12H,CH_2), 2.10(m,4H,CH_2), 2.30(t,4H,CH_2CO), 3.74(t,4H,OCH_2), 4.06(t,4H,CH_2N), 5.00(m,4H,CH_2=), 5.79(m,2H,CH=), 8.25(s,2H,ArH).

Bis-(N-allyl)pyromellitimide ***(2c),*** *bis-[N-(3-butenyl)]pyromellitimide* ***(2d)*** *and bis-[N-(4-pentenyl)]pyromellitimide* ***(2e):*** Stoichiometric amounts of pyromellitimide (2.16g, 10 mmol) and allyl bromide, 4-bromo-1-butene or 5-bromo-1-pentene were dissolved in 20 cm^3 of DMF. Then 20mmol of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was added and mixture was stirred at 60ºC over 2h. Then DMF was evaporated under reduced pressure. Residue was dissolved in $CHCl_3$ and extracted twice with 5% HCl and with water. Next chloroform was evaporated and crude product was crystallised from methanol.

2c: m.p. 222-24°C, [m.p. lit.(13) 215°C].

2d: Yield 3.0g (89%); m.p. 224-6°C. Elemental anal. ($C_{18}H_{16}N_2O_4$; 324.3): calc.; C 66,66, H 4.97, N 8.64, found: C 66.61, H 4.99. N 8.56. FTIR data (CH_2Cl_2, in cm^{-1}): 1773, 1723, 1393, 1360. ^{1}H NMR data ($CDCl_3$, in ppm): 2.47(m,4H,CH_2), 3.83(t,4H,N-CH_2), 5.06(m 4H,CH_2=), 5.77(m,2H,CH=), 8.26(s,2H,ArH).

2e: Yield 3.3g (90%). m.p. 203-4°C. Elemental anal. ($C_{20}H_{20}N_2O_4$; 352.4): calc.: C 68.17, H 5.72, N 7.95, found: C 68.22, H 5.77, N 8.02. FTIR data (CH_2Cl_2, in cm^{-1}): 1772, 1723, 1393, 1366. ^{1}H NMR data ($CDCl_3$, in ppm): 1.81(m,4H,CH_2), 2.12(m,4H,CH_2), 3.75(t,4H,N-CH_2), 5.01(m,4H,CH_2=), 5.80 (m,2H,CH=), 8.26(s,2H,ArH).



Scheme 2

Hydroquinone bis[(N-allylphthalimide)-4-carboxylate] ***(2f)***: *N*-allyltrimellitimide **(1f)** (10 mmol, 2.31g) and hydrochinone (5 mmol, 0.505g) were dissolved in 30 cm^3 of CH_2Cl_2 and then 3,1g (1.5mmol) of DCC was added. The mixture was stirred at room temperature for 6h. The crude product was isolated by standard procedure and crystallised from chloroform-benzene mixture. Yield 1.25g, 44%. m.p. 216-7°C. Elemental anal. ($C_{30}H_{20}N_2O_8$;): calc.: C 67.16, H 3.76, N 5.22, found: C 67.26, H 3.88, N 5.11. FTIR data (CH_2Cl_2, in cm^{-1}): 1774, 1749, 1716; ^1H NMR data ($CDCl_3$, in ppm): 4.36(m,4H, CH_2N), 5.25(m,4H,CH_2=), 5.60(m,2H,CH=), 7.35(s,4H_{ar}), 8.05(m,2H_{ar}), 8.60(m,2H_{ar}), 8.68(m,2H_{ar}).

*Copolyimides **3a-f:*** All polymers were synthesised according to the same method presented below. 1.1 Mmol of alkenylimide (**2a-f**) was dissolved under nitrogen in 10 cm^3 of dry toluene and then 1 mmol of 1,1,3,3,-tetramethyldisiloxane was added. After addition of a catalyst (10μl of 3% PTDD in xylene) the reaction was carried out for 24 h with magnetic stirring at room temperature. Then the temperature was raised and the process was continued for another 24 h at 40-45°C. A course of hydrosilylation was investigated by means of FTIR spectroscopy. The disappearance of Si-H absorption band (about 2160cm^{-1}) enables us to establish the end of reaction after 48 h. The polymers were purified by repeated dissolution in methylene chloride and precipitation in methanol (5-6 times) and finally dried under vacuum.

Measurements

FTIR spectra were recorded on a Perkin Elmer 2000 spectrometer in dichloromethane. ^1H NMR spectra were performed on a Gemini Varian 200 in $CDCl_3$. Melting points were taken in open capillary tubes on a Gallenkamp 5 melting point apparatus and were uncorrected. Molecular weights were determined by gel chromatography method (MIXED-C column, PS standards) using Shimadzu CR4A Chromatopac apparatus in THF. DSC studies were performed at a rate of 10°C/min. using DuPont 2100 calorimeter.

Results and discussion

The analytical data of polymers **3a-f** are presented in the Table 1. Typical ^{1} H NMR spectra of the polymer (**3a**) and the monomer (**2a**) are shown in Fig. 1. The comparison of these plots proves that terminal unsaturated bonds in monomers disappear almost completely during chain propagation. The reactions of hydrosilylation follow the anti-Markovnikov mechanism (β-addition) in the case of alkenylimides studied. We have found that only for allyl-ended monomers **2c** and **2f** trace amounts of α-adducts (identified by ^{1} H NMR) had been produced, too.

It must be admitted that the value of M_w of compounds obtained were not large (2850-6000u). Despite this fact the hydrosilylation appears to be a handy method for preparation of siloxane imides and this kind of condensation allows the application of new monomers for syntheses of silicon-modified polyimides. Oligomers obtained in this way are soluble in organic solvents such as aromatic hydrocarbons or halogen derivatives and show thermoplastic properties.

It seems interesting that polymer **3f** shows liquid crystalline phase; DSC measurements and microscopic observations confirmed existence of the mesophase in the range of 107-197°C. It should be noticed that similar structures of aromatic esters of trimellitimides had been postulated earlier as good mesogen groups (16-18).

Table 1. Analytical and spectroscopic data of copolyimides **3a-f**.

polymer 3	**Elemental analysi (%)**	**^{1}H NMR data δ (in ppm)**	**FTIR data (in cm^{-1})**	**m.p. (°C)**	**%**
a: $(C_{28}H_{38}N_2O_9Si_2)_n$ $(602.2)_n$	calc. C 55.79, H 6.36, N 4.65 found C 55.45, H 6.63, N 4.71	0.04(s,12H,SiCH$_3$), 0.50(m,4H,CH$_2$Si), 1.30-1.65 (m,12H, CH$_2$), 4.17 (t,4H, CH$_2$O), 4.49(s,4H, NCH$_2$), 8.35(s,2H,ArH)	1781,1754 1731,1410 1390,1254	135	43
b: $(C_{36}H_{54}N_2O_9Si_2)_n$ $(714.3)_n$	calc. C 60.48, H 7.62, N 3.92 found C 63.98, H 7.75, N 4.04	0.05(s,12H,SiCH$_3$), 0.41-0.67 (m, 4H, CH$_2$Si), 1.25-1.80 (m, 24H, CH$_2$), 2.29(t,4H, CH$_2$CO),3.73 (t, 4H, NCH$_2$), 4.04 (t,4H, COCH$_2$), 8.25(s,2H,ArH)	1772,1725, 1436,1393 1255	90	33
c: $(C_{20}H_{26}N_2O_5Si_2)$ $(430.6)_n$	calc. C 55.79, H 6.09, N 6.51 found C 54.98, H 5.93, N 6.22	0.04(s,12H,SiCH$_3$), 0.57-1.71 (m,8H,CH$_2$),3.70(t,4H,NCH$_2$), 8.23(s,2H,ArH)	1772,1724 1391,1360	160	64
d: $(C_{22}H_{30}N_2O_5Si_2)_n$ $(458.7)_n$	calc. C 57.61, H 6.59, N 6.11 found C 56.88, H 6.91, N 6.00	0.05(s,12H,SiCH$_3$) ,0.50-0.62 (m,4H,CH$_2$Si), 1.26-1.78 (m,8H,CH$_2$),3.72(t,4H,NCH$_2$), 8.24(s,2H,ArH)	1773,1723, 1393,1360	155	61
e: $(C_{24}H_{34}N_2O_5Si_2)_n$ $(486.7)_n$	calc. C 59.23, H 7.04, N 5.76 found C 58.78, H 7.22, N 5.52	0.04(s,12H,SiCH$_3$), 0.40-0.58 (m,4H,CH$_2$Si), 1.35-1.75 (m12H, CH$_2$), 3.72(t,4H,NCH$_2$), 8.24(s,2H,ArH)	1772,1723, 1394,1366	155	67
f: $(C_{34}H_{34}N_2O_9Si_2)_n$ $(678.1)_n$	calc. C 60.88, H 5.11, N 4.18 found C 61.81, H 6.78, N 4.00	0.05(s,12H,SiCH$_3$), 0.45-0.60 (m,4H,CH$_2$Si), 1.56(m,4H,CH$_2$), 3.70(t,4H,NCH$_2$), 7.34(s,4H,ArH), 8.00(m,2H,ArH), 8.61(m,4H,ArH)	1776,1744 1728	107 N 197 I*	34

***) temperatures of LC phase transition were determined by means DSC method on heating rate**

It is widely known that rubbed films of various polymers produce uniform homogeneous alignment of most liquid crystals which come into contact with them (19,20). Rubbed polyimide surfaces have been most often employed as orientating coatings (21,22). In this aspect poly(siloxane imide)s could offer such interesting possibility. Despite of modest M_w values, obtained PSIs show a good adhesion to glass and metal surfaces.

Our preliminary results have revealed very high ability of such coatings to align nematic liquid crystals (23). We believe that this findings justify our studies on synthesis of new poly(siloxane imide)s as materials for liquid crystalline displays preparation.

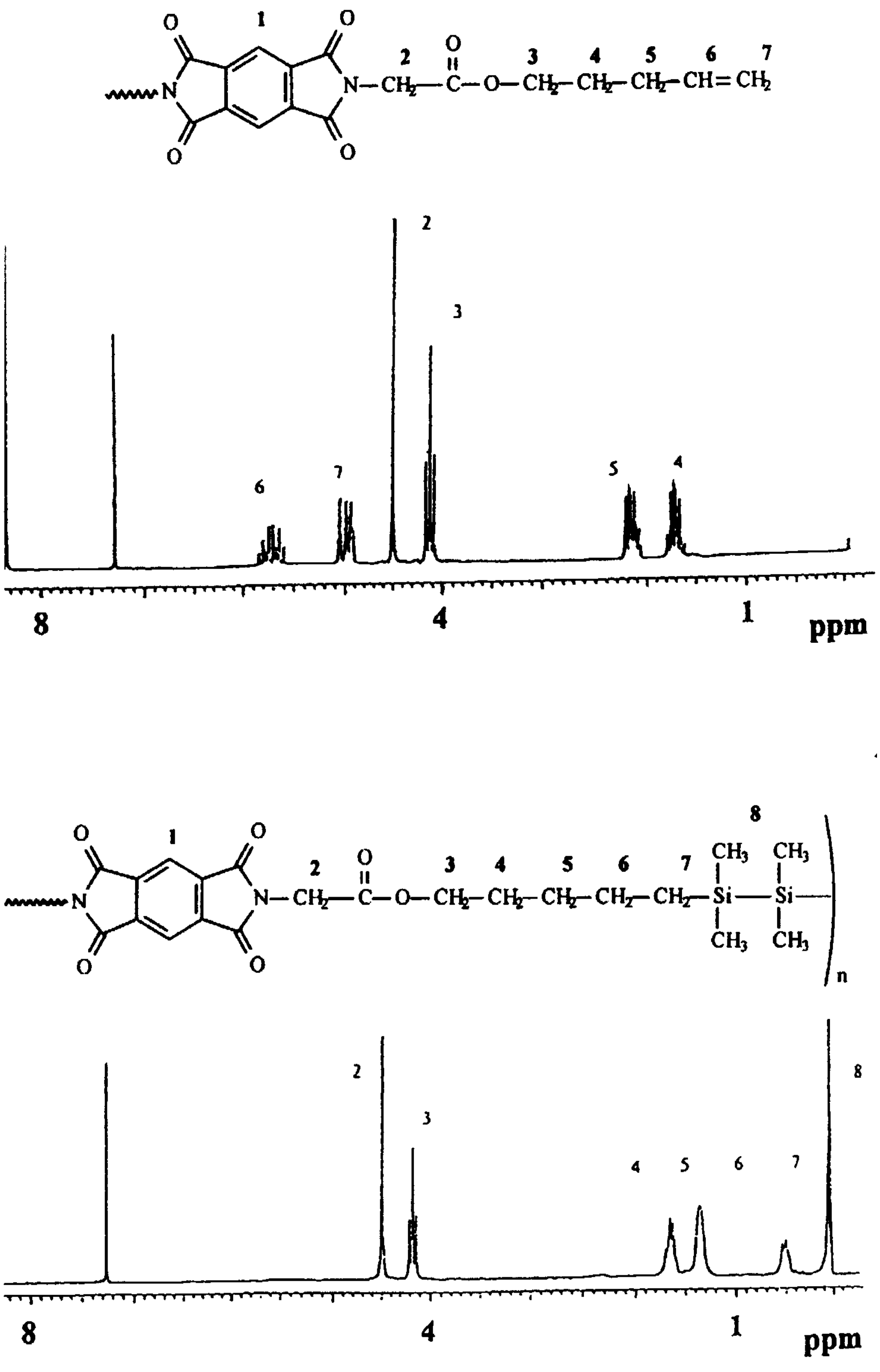


Figure 1. ^{1}H NMR spectra of monomer **2a** and PSI **3a**

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