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Synthesis and characterization of novel polyurethanes based on 4,4'-{1,4-phenylenebis[methylylidenenitrilo]} diphenol

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Summary

A series of novel segmented polyurethanes (PUs) containing imine units in the main chain were prepared by polyaddition reaction of various diisocyanates like 4,4′-diphenyl-methane diisocyanate, tolylene 2,4-diisocyanate, isophorone diisocyanate and hexamethylene diisocyanate with 4,4'-{1,4-phenylenebis[methylylidenenitrilo]} diphenol based diol. The structure of the diol and segmented PUs were determined by Fourier transform infrared, ultraviolet-visible spectrometry and fluoroscence spectroscopy. PUs were soluble is polar aprotic solvents. Thermal properties were done by using differential scanning calorimetry (DSC) and thermogravimetric analysis. DSC data display the PUs having multiple endotherm peaks. MDI based PU show the more thermal stable compared to other PUs.

Introduction

Segmented polyurethanes (PUs) and polyureas were found to be insoluble in acidic as well as organic solvents due to their rigid backbones [1,2], thereby inhibiting their applications due to difficulty in processing. In order to increase the solubility, the polymer structure modification is essential, wherein one can introduce the bulky or asymmetric groups on the polymer backbone or incorporate non-coplanar structural units on the main polymer chain [3-5]. Polymers containing conjugated moieties have been employed in photovoltaic devices, sensors, catalysis and batteries [6-8].

In our previous research [9-12], Schiff base based PUs, chalcone based PUs, azo-based PUs have been prepared using 2,2'-{ethane-1,2-diylbis(nitrilomethylylidene)} diphenol, 2,2'-{hexane-1,6-diylbis(nitrilo-methylylidene)}diphenol, 4-{[(4-hydroxyphenyl)imino] methyl}phenol, 2,6-bis(4-hydroxybenzylidene)cyclohexanone, 4,4’-[1,4-phenylenedi-diazene-2,1-diyl]bis(2-carboxyphenol) and 4,4’-[1,4-phenylenedi-diazene-2,1-diyl] bis(2-chlorophenol) with different diisocyanates. In present work, we describe the synthesis and characterization of novel PUs from the polyaddition between imine base diol 4,4'-{1,4-phenylenebis[methylylidenenitrilo]}diphenol with different diisocyanates like 4,4′-diphenylmethane diisocyanate (MDI), tolylene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI). The synthesized PUs were characterized by using Fourier transform infrared

(FTIR), UV-vis, fluoroscence spectroscopy. Thermal properties of the obtained PUs were investigated using differential scanning calorimetry (DSC) and thermogravimetry (TGA).

Experimental

Materials

Terephthalaldehyde, *p*-aminophenol, MDI, TDI, IPDI, HDI and dibutyltin dilaurate (DBT) were purchased from Aldrich (Milwaukee, USA) and were used without further purification. Ethanol, tetrahydrofuran, dimethyl formamide (DMF), dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and dimethylacetamide (DMAc) were all are of analytical reagent (A.R.) grade samples purchased from Fluka. All the solvents were purified before use by following the standard procedures.

Instruments

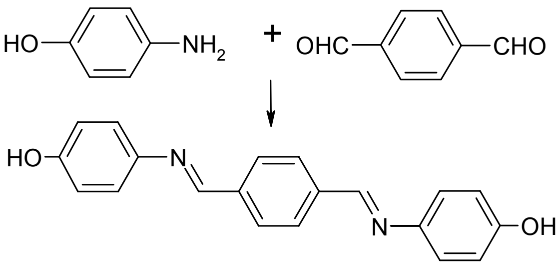
The FTIR spectral measurements were scanned between 400 and 4000 cm^{-1} using Nicolet (Model, Impact 410, Madison, WI, USA) spectrophotometer. UV-visible spectra (Secomam, France) were recorded in the wavelength range of 200-600 nm for dilute PU solution of 5×10^{-4} M prepared in a spectroscopic grade DMF solvent. Fluorescence spectra (F-2000, Japan) were also recorded in the wavelength range of 200-800 nm. Thermogravimetry (TGA) and differential scanning calorimetry (DSC) were recorded on a Perkin-Elmer Diamond analyzer (Shelton, USA) in the temperature interval from ambient to 800°C under a nitrogen flow rate of 20 mL/min. A sample of about 10 mg was placed in a platinum crucible to record TGA and DSC spectra against α-alumina at the heating rate of 10°C/min.

Preparation of 4,4'-{1,4-phenylenebis[methylylidenenitrilo]}diphenol (PBMD)

The mixture of terephthalaldehyde (6.7 g, 0.05 mol) taken in ethanol (75 mL) was stirred for 30 min. To this solution, 4-aminophenol (10.9 g, 0.1 mol) in ethanol (75 mL) was added, and the reaction mixture was stirred for 7 h at 70°C. After cooling the mixture to room temperature, the precipitate was filtered off. Recrystallization of the solid product was done by using ethanol. m.p. 309-310°C.

FTIR (KBr): 3383, 3030, 2872, 1621, 1597, 1501, 1442, 1358. 1248, 1188, 1103, 1006, 973, 887, 827, 766 and 708 cm^{-1}.

The reaction Scheme 1 displays the formation of PBMD based on the above cited spectral assignments.



Scheme 1. Preparation of 4,4'-{1,4-phenylenebis[methylylidenenitrilo]}diphenol.

Polyurethanes synthesis

A general procedure used to synthesize PUs was carried out in a three-necked 100 mL round bottom flask equipped with a magnetic stirrer, condenser and dropping funnel under dry nitrogen atmosphere. The diol 4,4'-{1,4-phenylenebis [methylylidene-nitrilo]} diphenol were dissolved in dry DMF under dry nitrogen atmosphere with a constant stirring and two drops of DBT catalyst were added. Then, equimolar quantity of diisocyanates (MDI, TDI, IPDI or HDI) with respect to diol taken in dry DMF was added to this solution over a period of 30 min. The reaction mixture was stirred continuously for 10 h at 75-80°C, cooled, poured into distilled water and then filtered. The solid powder dried under reduced pressure at 30°C. The chemical structures of PUs are shown in Scheme 2.

Preparation of poly[4,4'-{1,4-phenylenebis[methylylidenenitrilo]}diphenyl 4,4'- methylene diphenylene diurethane] (PU-1)

PU-1 was prepared by taking MDI (1.251 g, 0.005 mol) and PBMD (1.58 g, 0.005 mol) to yield 2.5 g (88 %). FTIR and TGA assignments are given below.
FTIR (KBr): 3300, 3032, 2921, 1647, 1619, 1591, 1550, 1504, 1449, 1413, 1303, 1234, 1104, 1010, 965, 834 and 709 cm^{-1}.
TGA: 10% weight loss is at 242°C and a 50 % weight loss at 707°C were observed. The residual weight at 800°C was 44 %.

Preparation of poly[4,4'-[4,4'-{1,4-phenylenebis[methylylidenenitrilo]}diphenyl, tolylene 2,4-diurethane] (PU-2)

PU-2 was prepared by taking TDI (0.871 g, 0.005 mol) and PBMD (1.58 g, 0.005 mol) to give a yield of 2.32 g (94 %). FTIR and TGA assignments are given below.
FTIR (KBr): 3303, 3025, 2921, 2864, 1654, 1619, 1593, 1547, 1503, 1450, 1382, 1305, 1245, 1103, 1006, 964, 876 and 837 cm^{-1}.
TGA: 10 % weight loss is at 233°C and a 50 % weight loss at 590°C were observed. The residual weight at 800°C was 45 %.

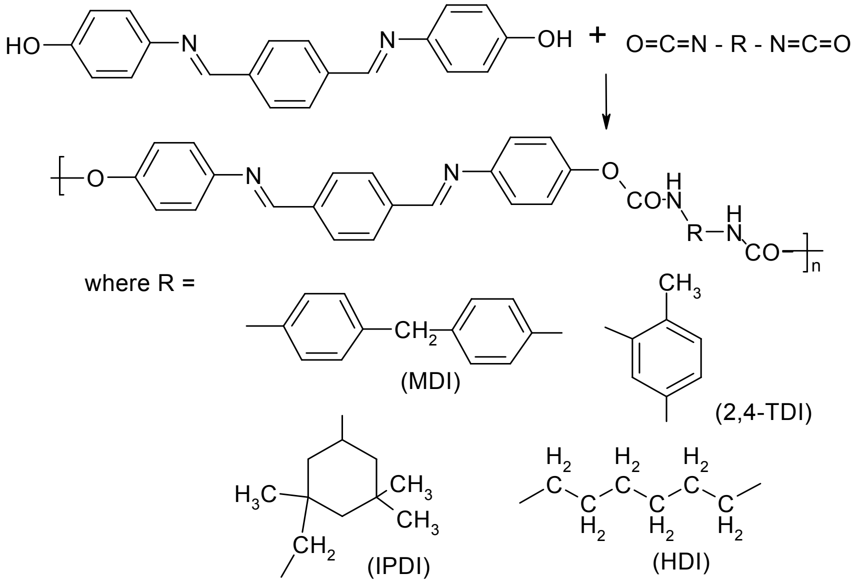
Preparation of poly[4,4'-[4,4'-{1,4-phenylenebis[methylylidenenitrilo]}diphenyl, isophorone diurethane])] (PU-3)

PU-3 was prepared by taking IPDI (1.11 g, 0.005 mol) and PBMD (1.58 g, 0.005 mol) to yield 2.51 g (93 %). FTIR and TGA assignments are given below.
FTIR (KBr): 3332, 3176, 2948, 2920, 1657, 1618, 1576, 1504, 1451, 1380, 1305, 1270, 1234, 1099, 964, 886 and 735 cm^{-1}.
TGA: 10 % weight loss is at 230°C and a 50 % weight loss at 586°C were observed. The residual weight at 800°C was 40 %.

Preparation of poly[4,4'-{1,4-phenylenebis[methylylidenenitrilo]}diphenyl, hexa-methylene 1,6-diurethane] (PU-4)

PU-4 was prepared by taking HDI (0.841 g, 0.005 mol) and PBMD (1.58 g, 0.005 mol) to yield 2.29 g (94 %). FTIR and TGA assignments are given below.
FTIR (KBr): 3315, 3158, 2933, 2858, 1697, 1654, 1617, 1577, 1504, 1450, 1383, 1233, 1096, 966, 875 and 836 cm^{-1}.

TGA: 10 % weight loss is at 202°C and a 50 % weight loss at 427°C were observed. The residual weight at 800°C was 28 %.



Scheme 2. Reaction pathways for the formation of PUs (i.e., PU-1 to PU-4).

Results and discussions

Spectral data

UV-visible and fluoroscence spectra of the PBMD and PUs were determined using DMF as a solvent at ambient temperature. The absorption and emission spectral data of both the PBMD and PUs are listed in Table 1. In the spectra of the Schiff based diol and PUs, the aromatic bands at 265 – 274 nm are attributed to benzene π - π^* transitions. The bands at 320-328 nm are assigned to azomethine π-π^* transitions. The emissions from these diol and PUs are appearing around 363 - 375 nm and 450 - 478 nm, on excitation at 270 and 325 nm, respectively. From the absorption and emission spectra, it is concluded that there is no significant difference in the diol and the PUs prepared. These data are agreement with our earlier reported datas.

Table 1. Absorption and emission peaks for diol and PUs

Sample	λ_{max} (nm)	
	Absorption	Emission
PBMD	270, 320	375, 469
PU1	265, 323	370, 466
PU2	269, 324	363, 450
PU3	265, 327	369, 478
PU4	274, 328	365, 475

The FTIR spectra of the PUs indicated the disappearance of hydroxyl (no absorption at 3383 cm^{-1}) / isocyanate (no absorption at 2270 cm^{-1}) groups and formation of the urethane linkage as shown in the Figure 1. In all the PUs, the sharp bands appearing between 1647 and 1697 cm^{-1} are due to the presence of hydrogen bonded carbonyl group [1]. However, hydrogen-bonded broad N-H groups of urethane are shown in the region from 3300 – 3383 cm^{-1}. The imine (CH=N) groups have appeared in the region 1617 – 1621 cm^{-1} [9].

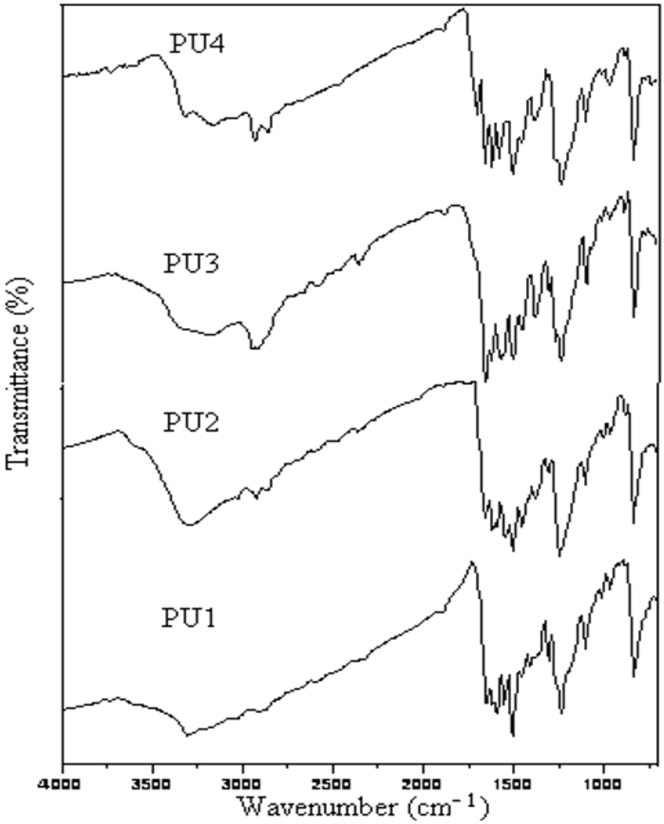


Figure 1. Representative FTIR spectra of PUs (PU1 to PU4).

Thermal properties

The DSC and TGA thermograms of all PUs are shown in Figures 2 and 3. The results are summarized in Table 2. The existence of multiple endotherms has been documented on thermal characteristics of the segmented PU block copolymers [13-15]. Martin et al. [16] suggested that five endotherms observed were possibly due to the melting of various hard segment length populations. Koberstein and Galambos [17] suggested that the origin of multiple endotherms in PUs is dependent upon the specimen preparation procedure. Blackwell and Lee [18] studied the multiple melting in MDI-based PUs that have been oriented and thermally annealed. On the other hand, van Bogart et al. [19] identified three endothermic transitions associated with the ordering of MDI/1,4-butanediol hard segments in materials subjected to the third thermal cycle. In the light of these reports, it is obvious that the melting behavior of PUs is highly dependent upon the procedure adopted for sample preparation. Indeed, the origin of multiple melting peaks are inherently different for materials prepared under varying conditions.

Table 2. Different melting endotherms from DSC

	PU1	PU2	PU3	PU4
T_1 ^{0}C	106	99	95	144
T_2 ^{0}C		207	292, 297	
T_3 ^{0}C	361	329	338	334

T_1 is the lowest temperature endotherm measure by DSC
T_2 is the intermediate temperature endotherm measure by DSC
T_3 is the melting temperature endotherm measure by DSC

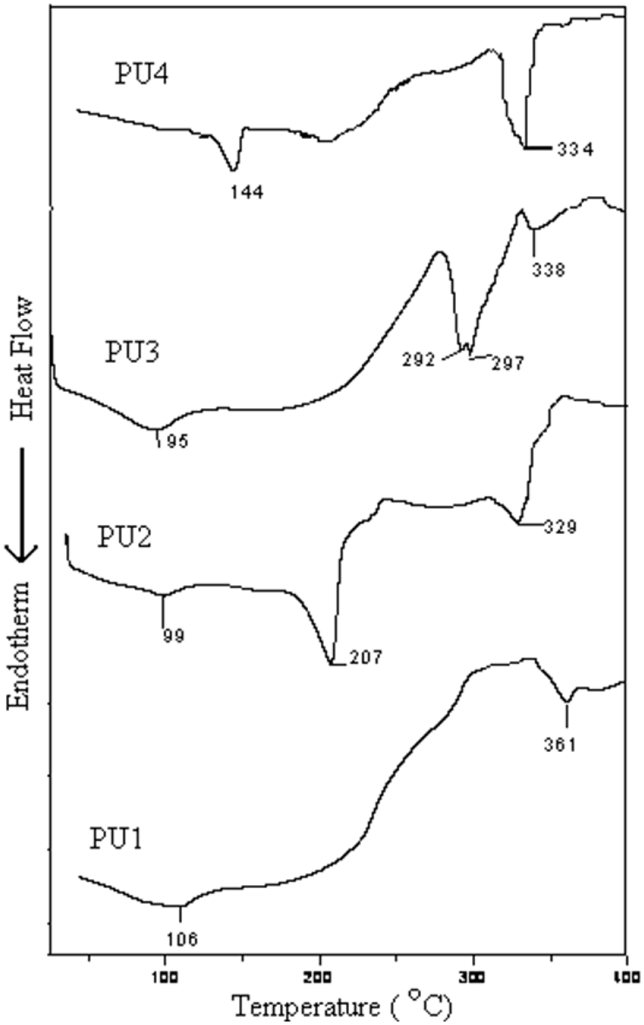


Figure 2. DSC thermograms of PU1 to PU4.

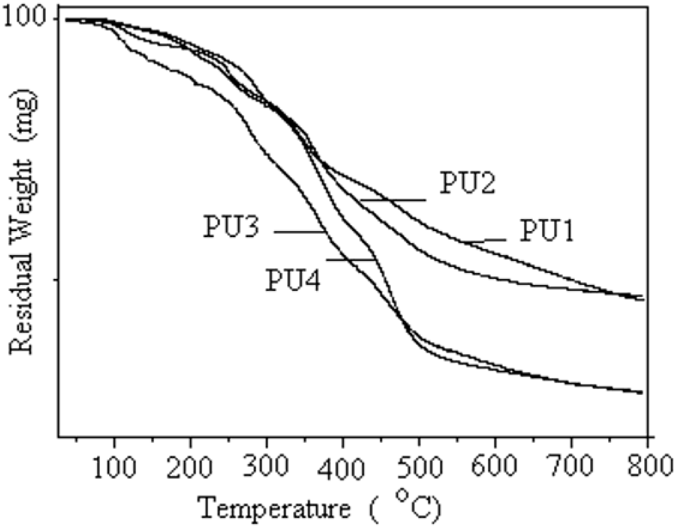


Figure 3. TGA tracings of PU1 to PU4.

In the present paper, we observed multiple melting phenomena in identical PUs prepared from only hard segments of the main chain. DSC data of PU-1 and PU-4, displayed two endothermic peaks, while PU-2 displayed three endotherms, but PU-3 and PU-4 exhibited four endotherms. The lowest endotherms (T_1) in the region of 95 -144°C was due to local restructuring of hard-segment units within the hard microdomains, which are considered to be the glass transition temperature, *Tg* of the PUs. However, the intermediate temperature endotherms (T_2) were observed around 207 -297°C, which were associated with the destruction of long-range order of the unspecified nature of the PUs. Higher temperature endotherms (T_3) observed in the range 329 -361°C can be generally ascribed to melting of the microcrystalline regions within the hard microdomains.

Weight loss data from TGA for all the PUs are shown in the Figure 3. These results suggested that 10 % and 50 % weight loss had occurred in the temperature range of 202 -242°C and 427 – 707°C, respectively. The residual weight remaining at 800°C was 28 to 45 %. This variation in weight loss was due to the differences in the structure of hard segments of PUs. TGA data indicated that the MDI-based PUs exhibited good thermal stability when compared to other diisocyanate based PUs, which is attributed to the presence of phenyl on the main chains.

Solubility properties

All the PUs were soluble in polar aprotic solvents such as NMP, DMAc, DMF and DMSO. Due to the presence of intermolecular hydrogen-bonding insoluble in low boiling solvents.

Conclusion

Novel PUs based on 4,4'-{1,4-phenylenebis[methylylidenenitrilo]}diphenol with MDI, 2,4-TDI, IPDI and HDI were synthesized. The structures of diol and PUs were confirmed by UV-visible, fluorescence and FTIR spectra studies. All the PUs were soluble in polar aprotic solvents and showed fluoroscent properties. DSC displayed the multiple endotherms that were in good agreement with the reported data. TGA indicated that the 10 % and 50 % weight loss has occurred in the temperature range of 202 - 242°C and 427 -707°C, respectively. The residual weight remaining at 800°C is about 28 to 45 %.

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