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Synthesis of segmented polyurethanes based on furazan units

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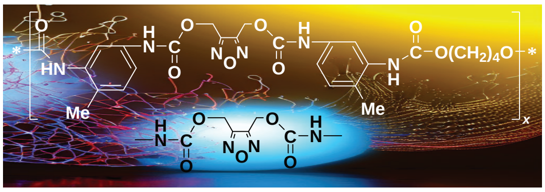
Linear polyurethane thermoplastics comprising furazan blocks soluble in organic solvents and having low melting points were obtained by nonequilibrium polycondensation of 3,4-bis(hydroxymethyl)furazan, butane-1,4-diol and 2,4-diisocyanatotoluene. The thermal behavior of some copolymers was studied by DSC and TGA methods.



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Furazan (1,2,5-oxadiazole) derivatives are the best studied among N,O-containing heterocyclic compounds.[1–4] The high enthalpies of formation of furazan (216 kJ mol^{-1}), its 2-oxide (furoxan, 226 kJ mol^{-1}), and, to a lesser extent, isomeric 1,3,4-oxadiazole (72.2 kJ mol^{-1}) allow one to expect that compounds based on them would also have good energy characteristics.[2] The chemistry of oxadiazoles makes it possible to create modern energy-rich components[1–6] and to expand the scope of biologically active compounds for agricultural and medical applications.[7,8]

However, the majority of oxadiazole-containing polymers is mainly based on 1,3,4-oxadiazole monomers.[9–11] The methods for the synthesis of these polymers involve two main approaches: (1) the two-step method with the preparation of polyhydrazides followed by their cyclodehydration (300–350 °C, 35 h, 1 Torr vacuum); and (2) the one-step method that requires condensing media such as polyphosphoric acid,[13] oleum, phosphorus pentoxide/methanesulfonic acid or an ionic liquid[14] to synthesize an 1,3,4-oxadiazole polymer by polycondensation. Studies on the synthesis of polymers with furazan units are much less common.[15,16]

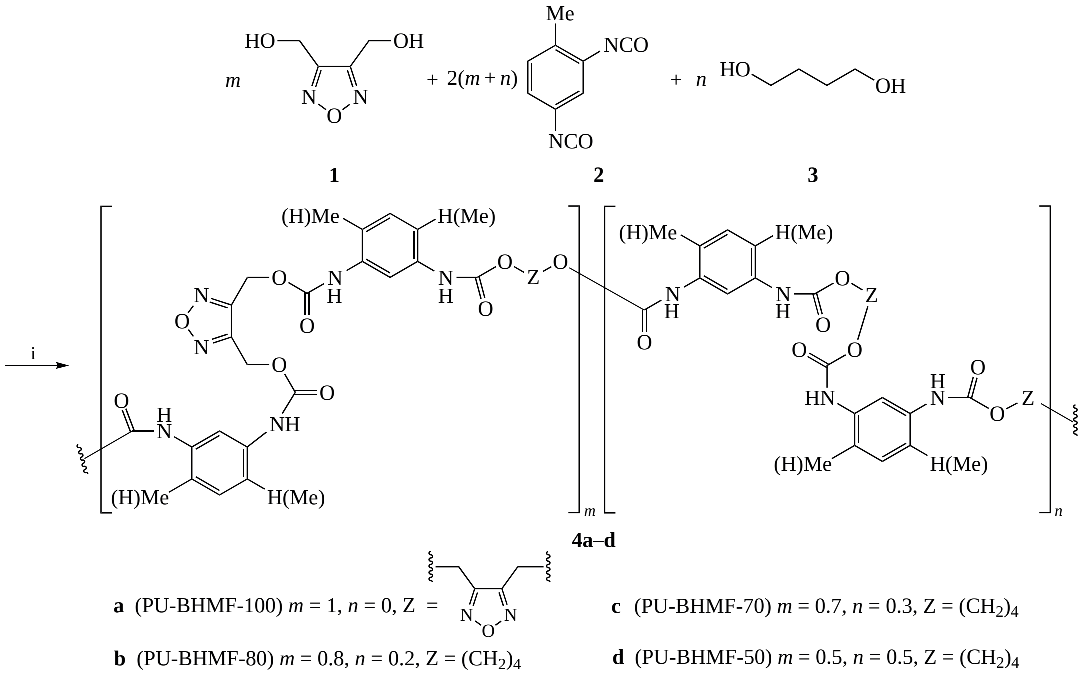
To synthesize polyheterocyclic structures, one should consider a high strain of their rings, while the presence of explosophore substituents significantly increases the sensitivity of these compounds, which would complicate the incorporation of such units into energy-rich formulations. The synthesis of poly(oligo)mers based on energy-rich monomers favors the formation of macromolecules with lower sensitivity, which simplifies their treatment and preserves the required thermodynamic characteristics.[17–21] Combining the beneficial thermochemical characteristics of the furazan ring and a flexible technique for the synthesis of polyurethane copolymers seems promising in the creation of new unique high-molecular compounds that would not only possess high energy-mass characteristics but also be prospective for utilization in up-to-date polymer-based light-emitting diodes.[22]

In this work, a novel convenient synthesis of linear polyurethane thermoplastics comprising furazan blocks, soluble in organic compounds (solvents) and having low melting point was developed. These compounds were obtained by a catalyst-free nonequilibrium polycondensation of 3,4-bis(hydroxymethyl)furazan[23] (BHMF) **1**, 2,4-diisocyanatotoluene **2** and butane-1,4-diol **3** (Scheme 1). For this goal, pre-melted BHMF **1** was successively mixed at 50 °C with diol **3** and diisocyanate **2**. The reaction was processed for 1.5 h with monitoring the intrinsic viscosity of the substance thus formed. Ethanol was used to terminate the reaction and for washing. The content of the BHMF units reflected in the abbreviated names of copolymers **4a–d**, namely, PU-BHMF-100/80/70/50, would correspond to the molar fraction of BHMF **1** reagent in the initial mixtures.

Preliminary experiments with di-*n*-butyltin dilaurate as a catalyst showed that the reaction gave three-dimensional cross-linked structures. In contrast, the same polycondensation of molten BHMF **1** in the absence of a catalyst (NCO/OH ratio of 1.0 : 1.0) at 50 °C affords soluble polyurethanes with linear structures. Characteristics of copolymers synthesized by this method are given in Table 1.

The choice of BHMF **1** is due to its both favorable formation enthalpy and ring stability. Despite the small size of this monomer, its reactivity and high reaction rate result in the formation of macromolecules with an intrinsic viscosity of 0.19–0.33 dl g^{-1}. These copolymers are soluble in cyclohexanone, DMSO, DMF and THF, and partially in EtOH. A regular increase in the density of the samples depending on their viscosity and the fraction of butane-1,4-diol **3** was observed. Moreover, sample **4c** possesses higher density than **4a**,**b** despite their comparable viscosity, which may be due to a stronger intermolecular interaction of the **4c** crystal domains formed.

The rather high acidity of the hydroxy groups in BHMF **1** favors its reaction with diisocyanate **2** to afford product **4a**. The changes in the IR absorption bands in the region of 3500–3300 cm^{-1} indicate that a reaction between the OH groups of diols and the NCO groups of diisocyanate occurs to form an urethane group NHCOO (NH 3347.71 cm^{-1}, OH 3400 cm^{-1} in the copolymer) with preservation of the furazan ring (1600,



1 **2** **3**

4a–d

a (PU-BHMF-100) $m = 1$, $n = 0$, Z =

b (PU-BHMF-80) $m = 0.8$, $n = 0.2$, Z = $(CH_2)_4$

c (PU-BHMF-70) $m = 0.7$, $n = 0.3$, Z = $(CH_2)_4$

d (PU-BHMF-50) $m = 0.5$, $n = 0.5$, Z = $(CH_2)_4$

Scheme 1 *Reagents and conditions*: i, stirring, 50 °C, N_2, 1.5 h.

Table 1 Properties of the synthesized polyurethane copolymers **4a–d**.

Product	Initial **1**/**3** molar ratio	Yield[a] (%)	[BHMF][b] (%)	MW$^{\text{unit}}$/g mol^{-1}	[η][c]/dl g^{-1}	d[d]/g cm^{-3}	ΔH_f (calc.)/kJ mol^{-1}	Ω[e] (%)
4a	100/0	98	100	608.5	0.191	1.121	699.2	–160.4
4b	80/20	99 (91)	71	592.5	0.194	1.125	602.5	–152.2
4c	70/30	97 (85)	56	584.5	0.186	1.215	597.0	–149.1
4d	50/50	98 (84)	38	568.5	0.332	1.238	538.0	–141.9

[a] Yield after washing is given in parentheses. [b] The actual content of furazan units according to ^{1}H NMR. [c] Intrinsic viscosity of a solution in cyclohexanone. [d] From the pycnometry. [e] Oxygen balance based on CO_2 for compound $C_aH_bN_cO_d$, Ω (%) = $1600 \times (d - 2a - b/2)$/MW (MW is molecular weight).

Table 2 Results of DSC/TGA analysis of the samples of polymers **4a–d**.

Product	mp/°C	T_{10}[a]/°C	$T_{\text{decomp.}}$/°C	
			start	intense
4a	137.8	252	258	298.5
4b	66.7	271	257	299.3
4c	65.7	259	266	303.8
4d	66.3	281	270	314.1

[a] Temperature corresponding to a mass loss of 10%.

881 cm^{-1}). In the ^{1}H NMR spectra, characteristic signals (4.12, 5.67–5.76 ppm) of the macromolecule were detected. They are present in the spectra of the entire series of copolymers, reflecting the structure of the terminal chain units predominantly formed from BHMF **1**.

Presumably, diisocyanate **2** reacts with butanediol **3** more readily than with BHMF **1** (see Table 1) since the actual content of furazan units in the products **4b–d** is somewhat lower than in the initial loadings. The results of calculations on the actual segment ratio in the copolymers according to ^{1}H NMR spectra showed that with a decrease in the content of furazan units in the copolymer, the competing role of butanediol **3** in the formation of the polyurethane chain increases. This explains the structure of the terminal units.

Polyurethane thermoplasts **4a–d** consisting of furazan-3,4-diylbis(methylene) and tetramethylene segments would form $(AB)_n$ structures.[24] The deviations in the results of C,H,N-elemental analysis, compared to the calculated ones, are within satisfactory limits, which is typical of high-molecular compounds and proves the assumed macromolecule structure based on data obtained by the set of spectral methods.

DSC and TGA data (Table 2) show that samples **4b–d** have rather low melting points of about 65–66 °C, the sample **4a** being an exception (mp 137.8 °C). High melting point of polymer **4a** is due to the presence of rigid crystalline blocks in the chain consisting of both furazan units and urethane moieties. The calorimeter lines on the DSC thermograms have a slope because the compound volume inside the cell would change when thermoplastic elastomer crystals pass into a melt. The TGA thermograms of a series of polyurethane samples have similar shapes. Intense mass loss of the samples begins above ~257 °C. Below this temperature, the samples lose only 1–3 mass%, probably due to the loss of adsorbed moisture and other volatile components. In the temperature range of 260–380 °C, intense mass loss occurs due to direct thermal degradation. A ten-percent mass loss for the series of polymers is observed starting from 260 °C, which characterizes their high thermal stability. The two peaks in the degradation region of the DSC thermograms (257–300 °C) apparently indicate that the degradation process follows two possible thermal destruction mechanisms. However, it can also be due to two consecutive reaction stages, thus additional kinetic studies of thermal destruction are required. As the content of furazan units in the copolymer samples increases, the temperature of decomposition start decreases regularly to reach a minimum of 257 °C in the case of **4a**.

To conclude, the discovered reactivity of 3,4-bis(hydroxymethyl)furazan **1** in polycondensation opens prospects for synthesizing a series of urethane copolymers. The thermochemical characteristics of these materials with low melting points and high thermal stability may be of interest for the targeted creation of polymer formulations with a set of demanded physicochemical and mechanical properties.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.04.034.

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