

Synthesis and static light scattering studies of hairy rod polymers containing 1,3,4-oxadiazole rings in the repeating units

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Three new 'hairy' polymers containing 1,3,4-oxadiazole rings in the repeating units have been prepared and investigated by static light scattering. The two polymers of rod-like structure of the main chain show evidence of the same aggregation phenomena as other well known hairy rod polymers. The dimensions of the aggregates increase with increasing the polarity of the solvent. No aggregation occurs in the solution of the third polymer whose spacers, connecting the conjugated segments, are longer. This probably is determined by the increased flexibility of the polymer backbone. The third polymer, though hairy, has no rod-like structure of the main chain. Obviously, the rod-like structure is the determining factor for the aggregation observed.

Key words: hairy rod polymers; 1,3,4-oxadiazole ring; static light scattering.

INTRODUCTION

Hairy rod polymers, unlike the flexible random coil polymers, exhibit unique behaviour due to which nowadays they have often been investigated. These novel materials have good prospects for scientific and technological applications [1, 2]. Wegner and co-workers [3–5] have synthesised poly(*p*-phenylenes) with a large variety of side groups and investigated their properties. One of the major problems in the molecular characterisation of these polymers is their tendency to aggregate in solutions [6].

Most of the hairy rod polymers are substituted poly(*p*-phenylenes). It is well known however that the 1,3,4-oxadiazole ring exhibits the same electronic properties as the benzene ring [7]. Polymers, containing 1,3,4-oxadiazole rings, linked with unsaturated building units exhibit the typical properties of conjugated polymers [8]. Polymers with these rings have the advantage, however, to be more easily prepared than the corresponding polymers containing benzene rings.

The aim of this paper was to prepare a new class of hairy rod polymers containing 1,3,4-oxadiazole rings in the main chain and to investigate the influence of the length of the conjugated segments and their spacers on the aggregation phenomena.

EXPERIMENTAL

General methods

N-methylpyrrolidone (NMP) and N,N-dimethylformamide (DMF) (both from Fluka) were dried over phosphorus pentoxide and vacuum distilled. LiCl (Fluka) was dried at 130°C for 3 hrs. Terephthaloyl chloride and hydrazine sulphate (both from Fluka) were used without any further purification. 10% solution of phosphorus pentoxide in methanesulphonic acid (PPMA) was prepared from AR purity reagents (Fluka). All new polymers were characterised by ¹H NMR, FT-IR and elemental analysis. The ¹H NMR spectra were recorded on a Bruker 250 MHz instrument. Chemical shifts are reported in ppm using tetramethylsilane as an internal standard. The FT-IR spectra were taken as KBr pellets on a Bruker Vector 22 spectrometer. Gel permeation chromatography measurements were performed on a Waters 244 instrument. The number average molecular weight M_n was determined using monodisperse polystyrene standards. Columns of Ultra-Styrigel were used with pore sizes of 100 and 500 Å at 45°C, eluent THF.

Static light scattering (SLS)

The refractive index increments (dn/dc) of polymer solutions in DMF were measured by using a Brice-Phoenix Differential Refractometer BP-2000-V.

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Brice-Phoenix Universal Photometer 2000 with light source, high-pressure mercury vapour lamp ($\lambda_0 = 578$ nm) was used for the static light scattering experiments. Scattering intensities were measured with photomultiplier over an angular range between 45 and 135°, at three temperatures, 25, 40 and 55°C.

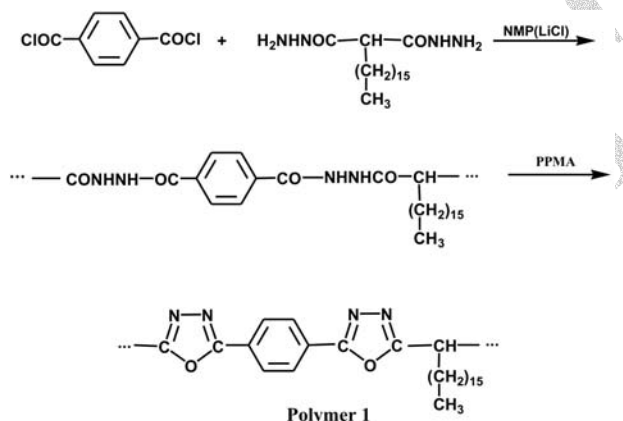
The same measurements were carried out on a multi-angle laser light scattering detector DAWN DSP Laser Photometer (Wyatt Technology Corp.).

Synthetic procedures

Dihydrazide of hexadecylmalonic acid. To 6.38 g (16.6 mmol) diethylester of hexadecylmalonic acid (obtained acc. [9]), dissolved in 10 ml *n*-butanol, was added slowly a solution of 2.08 g (41.5 mmol) hydrazine hydrate. The mixture was heated under stirring at 100°C for 4 h. After cooling, the crystals were filtered and recrystallised from ethanol. Yield 4.90 g (83%). M.p. 128–130°C.

$^1\text{H NMR}$ ($\text{C}_2\text{D}_2\text{Cl}_4$, ppm): $\delta = 8.82$ (s, 2H, NH); 4.22 (s, 4H, NH_2); 2.93 (t, 1H, CH); 1.67 (m, 2H, αCH_2); 1.21 (m, 28H, CH_2); 0.90 (t, 3H, CH_3).

Anal. calc. for $\text{C}_{19}\text{H}_{40}\text{N}_4\text{O}_2$ (%): C, 64.00; H, 11.32; N, 15.71; Found: C, 64.11; H, 11.61; N, 15.33.



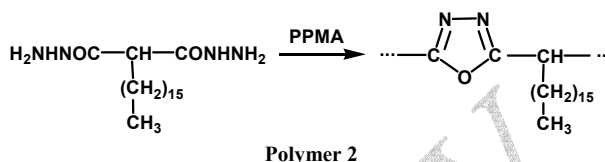
Scheme 1. Synthesis of polymer 1.

Synthesis of polymer 1. (Scheme 1). A mixture of 3 g (8.43 mmol) dihydrazide of hexadecylmalonic acid, 28.1 ml *N*-methyl-pyrrolidone and 1.45 g LiCl was stirred at room temperature under nitrogen to complete dissolution. The solution was then cooled to 0°C and 1.71 g (8.43 mmol) terephthaloyl chloride were added in portions. The stirring was continued at this temperature for 1 h and at room temperature for another 6 h. The clear viscous solution was poured slowly in water under stirring. The precipitated polymer was filtered, washed with water and dried. It was dissolved then in 30 ml PPMA and stirred with heating under argon at 90°C for 3 h. After cooling the reaction mixture was poured in water. The precipitate was filtered,

washed with water and dried. Yield 3.8 g (94%). $M_n = 6900$, $M_w = 9800$.

$^1\text{H NMR}$ ($\text{C}_2\text{D}_2\text{Cl}_4$, ppm): $\delta = 8.11$ (s, 4H, ArH); 2.78 (t, 1H, CH); 2.37 (m, 2H, αCH_2); 1.16 (m, 28H, CH_2); 0.84 (t, 3H, CH_3).

Anal. calc. for $(\text{C}_{27}\text{H}_{38}\text{N}_4\text{O}_2)_n$ (%): C, 71.96; H, 8.50; N, 12.43; Found: C, 70.82; H, 8.81; N, 12.09.

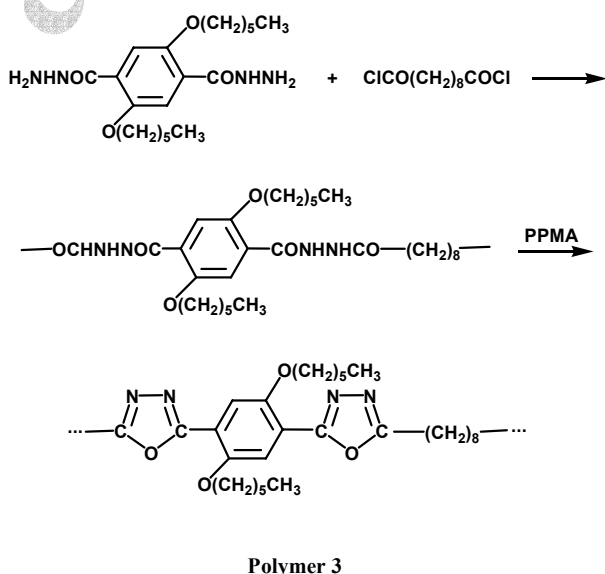


Scheme 2. Synthesis of polymer 2.

Synthesis of polymer 2. (Scheme 2) 3.00 g (8.43 mmol) dihydrazide of hexadecylmalonic acid and 1.2 g (0.009 mmol) hydrazine sulphate were dissolved in 90 ml PPMA. The solution was stirred for 30 h at 80°C, then cooled and poured in water. The polymer was filtered, washed with water and dried. Yield 3.00 g (93%). $M_n = 2450$, $M_w = 3200$.

$^1\text{H NMR}$ ($\text{C}_2\text{D}_2\text{Cl}_4$, ppm): $\delta = 3.05$ (t, 1H, CH); 1.67 (m, 2H, αCH_2); 1.22 (m, 28H, CH_2); 0.85 (t, 3H, CH_3).

Anal. calc. for $(\text{C}_{19}\text{H}_{34}\text{N}_2\text{O})_n$ (%): C, 74.46; H, 11.18; N, 9.14; Found C, 74.11; H, 11.59; N, 8.95.



Scheme 3. Synthesis of polymer 3.

Synthesis of 2,5-dihexyloxyterephthalic acid diethyl ester. It was prepared by Kossmehl and co-workers [10].

Synthesis of 2,5-dihexyloxyterephthalic acid dihydrazide. 8.6 g (0.02 mol) 2,5 dihexyloxyterephthalic acid diethyl ester dissolved in 40 ml ethanol were added dropwise for 2 h, with stirring at 80°C to 8.7 ml hydrazine hydrate (0.18 mol) dissolved in 65 ml ethanol. Heating was continued

for another 6 h. After cooling a white solid precipitated. It was recrystallised from water-ethanol (1:1) mixture, M.p. 98°C. Yield 5.8 g (73.6%).

¹H-NMR (DMSO-d₆, ppm): δ = 9,22 (s, 2H, CONH); 7,33 (s, 2H, Ar H); 4,577 (s, 4H, NH₂); 4,05 (t, 4H, OCH₂); 1,7 (m, 4H, OCH₂CH₂); 1,32 (m, 12H, CH₂); 0,87 (t, 6H, CH₃).

Anal. calc. for C₂₀H₃₄N₄O₄ (%): C, 60.89; H, 8.69; N, 14.20; Found C 60.45; H, 8.67; N, 13.91.

Synthesis of polymer 3 (Scheme 3). 1.86 ml (0.008 mol) sebacyl chloride were added slowly with stirring to ice-cooled solution of 2.5 g (0.0063 mol) 2,5-dihexyloxyterephthalic acid dihydrazide in 42 ml N-methylpyrrolidone. The mixture was stirred for 6 h and poured in water with stirring. The precipitate was filtered, washed with water and dried. It was dissolved then in 30 ml PPMA and stirred with heating under argon at 75°C for 24 h. After cooling, the solution was poured in water. The polymer was filtered, washed and dried. Yield 2.72 g (86.8%). $M_n = 150\,000$, $M_w = 162\,000$.

¹H-NMR (CDCl₃, ppm): δ = 7.67 (s, 2H, ArH); 4.10 (t, 4H, OCH₂); 2.90 (t, 4H αCH₂); 1.87 (m, 4H, OCH₂CH₂); 1.34 (m, 24H CH₂); 0.89 (t, 6H, CH₃).

Anal. calc. (%) for (C₃₀H₄₄N₄O₄)_n: C, 68.67; H, 8.45; N, 10.68; Found: C, 68.90; H, 8.22; N, 10.33.

RESULTS AND DISCUSSION

Three new polymers (**1–3**) with structure designed for our investigations have been prepared. The polymers contain 1,3,4-oxadiazole rings in their repeating units. The conjugated segment in polymer **1** consists of one benzene and two 1,3,4-oxadiazole rings. The segments are connected with very short spacers (CH-group). The conjugated segment in polymer **2** consists of only one 1,3,4-oxadiazole ring. Here the spacer is the same (CH-group). Consequently, the macromolecules of polymer **1** differ from the macromolecules of polymer **2** in the length of the conjugated segment. Due to the very short spacer in polymers **1** and **2** their macromolecules represent typical rigid rods. In order to increase their solubility, side chains are attached to the main polymer chain, therefore, these polymers belong to the class of hairy rod polymers. Polymer **3** contains conjugated segments connected by long flexible spacers with eight methylene groups. This polymer has the same conjugated segments as polymer **1**. In order to get solubility the benzene rings are substituted in this case. We prepared this polymer especially since it is 'hairy', but its main chain has not rod-like structure.

Polymers **1–3** were prepared via two different synthetic procedures. For polymers **1** and **3** we

applied the two-step method for 1,3,4-oxadiazole ring preparation proposed by Frazer *et al.* [11, 12]. First we prepared polyhydrazides, which were then cyclised to 1,3,4-oxadiazole ring containing polymers. Frazer *et al.* performed the cyclisation in polyphosphoric acid. We used instead a reagent made by dissolving 10% of phosphorus pentoxide in methanesulphonic acid since Ueda *et al.* [13] have shown that it exhibits similar chemical reactivity as polyphosphoric acid but with higher effectiveness. Polymer **2** was prepared according to the direct method of Iwakura *et al.* [14].

The characterisation of polymers **1** and **2** was done in dilute solutions in DMF using static light scattering (SLS) measurements. The results of the SLS measurements were compared to the SLS measurements of the segmented polymer **3** whose repeating unit differs from the repeating units of the other two polymers in the length of the spacers connecting the conjugated segments.

The refractive index increments dn/dc of polymers **1–3** in DMF at 578 nm wavelength of the incident light are given in Table 1.

Table 1. Refractive index increment dn/dc (ml·g⁻¹) of polymers **1–3** in DMF.

Polymer	1	1 ^a	2	3
Index	0.1107	0.0745	0.0875	0.1535

^a - Refractive index increment of polymer **1** in DMF + 3% LiCl.

Static light scattering was used to determine the weight average molecular weight M_w . Zimm plots were constructed making use of the Rayleigh-Gans-Debye equation [15]:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} \left(1 + \frac{q^2 \langle R_g^2 \rangle}{3} \right) + 2A_2c, \quad (1)$$

with

$$K = \frac{4\pi^2 n^2}{N_A \lambda_0^4} \left(\frac{dn}{dc} \right)^2, \quad (2)$$

$$q = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2}, \quad (3)$$

where the Rayleigh ratio R_θ depends on the intensity of scattered light at different scattering angles θ , c is the polymer concentration, q – magnitude of the scattering wave vector, $\langle R_g^2 \rangle$ – the mean square radius of gyration of the particles, A_2 – the second virial coefficient, n – the refractive index of the solvent, λ_0 – the wavelength of incident light in a vacuum, and N_A – the Avogadro constant.

The problem of SLS measurement in coloured solutions was solved by correction of the Rayleigh ratios R_θ of measured intensities of scattered light using the method proposed by Brice and co-workers [16].

One of the ways to analyse the results of the SLS is by using the Zimm plots. With this method, we can obtain the values of $\langle R_g^2 \rangle^{1/2}$, M_w and A_2 in a single chain. But when the polymer solutions represent complex systems, which, besides unimers, contain aggregates larger than the usual Zimm plot can provide, only the information of the polymer mixture, containing both the unimers and the aggregates could be obtained. Therefore, the appearance of aggregation phenomena in both hairy rod polymers **1** and **2** was studied through the acquired values of M_w and $\langle R_g^2 \rangle^{1/2}$ of the particles in the system.

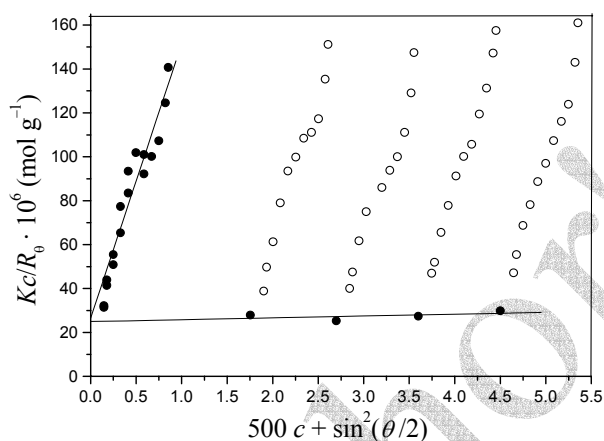


Fig. 1. Zimm plot of polymer **1** in DMF at 25°C.

Figure 1 shows one of the constructed Zimm plots for polymer **1** from which the values for $\langle R_g^2 \rangle^{1/2}$, M_w and A_2 have been calculated and are given in Table 2 together with the values of these parameters for polymer **2**. The values for M_w and $\langle R_g^2 \rangle^{1/2}$ for both polymers are high and point to the presence of large aggregates.

Similar results have been obtained from the SLS measurements on poly (*p*-phenylenes) made by Fytas and co-workers [17]. These authors support the idea that rigid rods are aggregated into small units, probably trimers, under these conditions. With the increase of temperature the solvent quality also increases, which can be seen from the values of A_2 for both hairy rod polymers, which suggests that this system becomes more strongly interacting as the temperature is reduced. These interactions in the

system enable the dimensions of the aggregates to decrease with the temperature increase, which can be seen from the values for M_w and $\langle R_g^2 \rangle^{1/2}$.

Table 2. Weight average molecular weights M_w , radius of gyration $\langle R_g^2 \rangle^{1/2}$ of the particles and second virial coefficient A_2 of polymers **1–3** at different temperatures.

Polymer	T, °C	M_w , kg·mol ⁻¹	$\langle R_g^2 \rangle^{1/2}$, nm	$A_2 \times 10^4$, mol·ml·g ⁻²
1	25	37.8	310.9	2.1
	40	35.5	193.9	2.6
	55	32.9	121.9	11.1
	40	76.3 ^a	83.0 ^a	-0.1 ^a
2	25	75.2	114.3	5.7
	40	66.4	124.1	10.7
	55	56.2	135.7	11.6
3	25	157.7	140.2	1.9
	40	150.1	150.4	9.7
	55	155.4	151.5	16.8

^a - Results of polymer **1** in DMF + 3% LiCl.

Comparing the values for M_w and $\langle R_g^2 \rangle^{1/2}$ for polymers **1** and **2** it can be concluded that polymer **2** forms larger aggregates in its solutions than the aggregates present in polymer **1** solutions. Most probably this phenomenon is determined by the higher rigidity of its molecular backbone compared with that of polymer **1**. This is also confirmed by the fact that the size of the aggregates in polymer **1** increases with the increase of the polarity of the DMF solvent caused by adding 3% LiCl. Also in this system the second virial coefficient A_2 (Table 2) has a negative value. These results suggest that the solvent quality is not good.

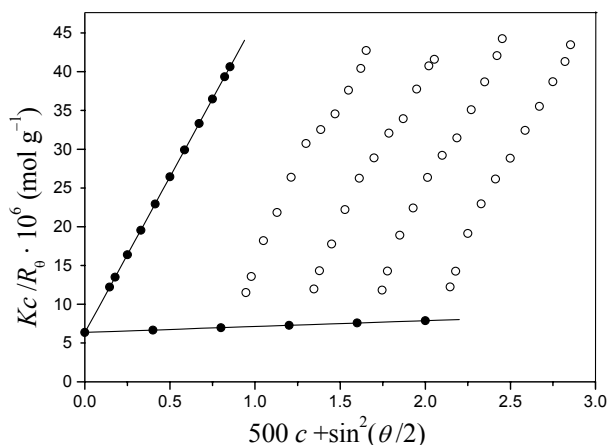


Fig. 2. Zimm plot of polymer **3** in DMF at 25°C.

Unlike polymers **1** and **2**, polymer **3** does not form aggregates in diluted DMF solutions. This can be seen from the shape of the constructed Zimm plots. One of these is shown in Fig. 2. Also, the

acquired values for M_w and $\langle R_g^2 \rangle^{1/2}$ at all three temperatures in Table 2 correspond to values of a single chain. The values of the second virial coefficient A_2 are positive and show that DMF is a good solvent for this polymer.

In conclusion, apart of the fact that polymer **3** contains the same conjugated segment in the repeating unit as polymer **1**, it does not aggregate. This is obviously due to the longer flexible spacers. In this polymer by bending the flexible spacers enable approaching of the conjugated segments [18]. Here the flexibility of the macromolecule is enhanced also by the higher molecular weight. Polymers **1** and **2**, however, obviously due to the short spacers, have aggregation specific for the hairy rod polymers. The cause for this aggregation is not only the presence of the flexible side chains but the rod-like structure of the polymer backbone.

CONCLUSIONS

Polymers **1** and **2** containing 1,3,4-oxadiazole rings in their repeating units exhibit the same aggregation phenomena as other well known hairy rod polymers [6]. The dimensions of the aggregates increase with increasing the polarity of the solvent. No aggregation occurs in the solution of the third polymer whose spacers, connecting the conjugated segments, are longer. This probably is determined by the increased flexibility of the polymer backbone. The third polymer, though hairy, has not rod-like structure of the main chain. Obviously, the rod-like structure is the determining factor for the aggregation observed.

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СИНТЕЗА И ИЗСЛЕДВАНЕ СЪС СТАТИЧНО СВЕЛТОРАЗСЕЙВАНЕ НА ОКОСМЕНИ
ПРЪЧКОВИДНИ ПОЛИМЕРИ, СЪДЪРЖАЩИ 1,3,4-ОКСАДИАЗОЛОВИ ПРЪСТЕНИ В
ПОВТАРЯЩИТЕ СЕ ЗВЕНА

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(Резюме)

Синтезирани са три нови „окосмени“ полимери, съдържащи 1,3,4-оксадиазолови пръстени в повтарящите им се звена и са изследвани със статично светлоразсейване. Двата полимера с пръчковидна структура на главната верига показват същото явление на агрегиране както и други добре известни окосмени пръчковидни полимери. Размерите на агрегатите нарастват с увеличаване на полярността на разтворителя. В разтвора на третия полимер, на когото спейсърите, свързващи спрегнатите сегменти са по-дълги, не протича агрегиране. Това вероятно се определя от увеличената гъвкавост на тази полимерна верига. Третият полимер, макар и окосмен, няма пръчковидна структура на главната верига. Очевидно пръчковидната структура е определящия фактор за наблюдаваното агрегиране.