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4-Nitrophenylhydrazone of poly(4-formylstyrene)

Ivan Kmínek*, Danica Diskočilová, Jaroslav Straka, Stanislav Nešpůrek

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
CZ-162 06 Prague 6, Czech Republic

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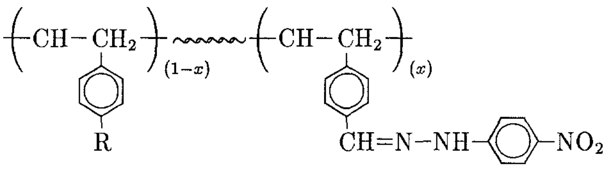
Summary

The title polymer was prepared by the reaction of poly(4-formylstyrene) with 4-nitrophenylhydrazine. The polymer is amorphous and possesses a glass transition temperature $T_g = 230$ °C. It crosslinks both thermally and by UV-irradiation and forms dense networks when heated above T_g. All these properties make the polymer suitable for a stable poled system. However, a quite rapid thermal decay (bleaching) of the bound chromophore precludes the material from using in nonlinear optics.

Introduction

In the past several years much effort has been devoted to poled polymeric systems usable in nonlinear optics (NLO) (1). For practical applications the poled system needs to be stable at 80–100°C in air for several years. This requirement implies use of polymers with high glass transition temperature, T_g, or crosslinkable materials (1).

In a preliminary communication (2) we have reported on the properties of 4-nitrophenylhydrazones of partially formylated polystyrene (degree of substitution $x = 0.03$ to 0.13, R = H):



Such polymers, the preparation of which is comparatively easy and cheap, crosslink thermally and/or by UV-irradiation in the solid state through the hydrazone groups. These substituents, therefore, might conveniently serve both as NLO-chromophores and crosslinking "agents" (1). Notably, the chromophore groups also undergo some bleaching of an unknown mechanism during thermal treatment (or

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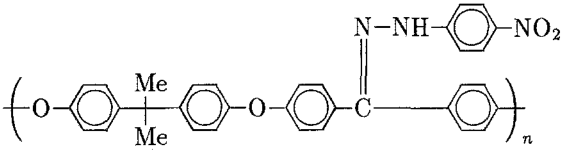
* Corresponding author

UV-irradiation). T_g of the polymers rises quite steeply with the degree of substitution ($T_g = 82.8°C$ for $x = 0$ and $T_g = 139.0°C$ for $x = 0.13$). We assumed that polymers of this type with much higher x could possess very high T_g and could be highly crosslinkable thus fulfilling the requirements for a stable system after poling. This idea has been further supported by a recent communication (3) on 4-nitrophenylhydrazone of Bisphenol K/Bisphenol A copolyether (NBPE):



The poled samples of NBPE exhibited stable NLO activity for 3.8 years at 100°C.

In this paper the synthesis and properties are described of 4-nitrophenylhydrazone of poly(4-formylstyrene) ($x > 0.9$, R = CHO).

Experimental

Poly(4-formylstyrene) was obtained using spontaneous thermal bulk polymerization of 4-formylstyrene (4) near its boiling point. The resulting material exhibits a broad distribution of molecular weights (typically, $M_n = 56\,000$, $M_w = 280\,000$), as determined by SEC in tetrahydrofuran (THF).

4-Nitrophenylhydrazone of poly(4-formylstyrene) (PFSN) was prepared by boiling 1 g (7.5 mmol) of the polymer dissolved in 100 ml of DMF/THF mixture (1 : 1 by volume) with 3 g (19.6 mmol) 4-nitrophenylhydrazine and 0.8 g (4.2 mmol) p-toluenesulfonic acid or 10 ml concentrated HCl for 30 min. The polymer was then precipitated with water solution of $NaHCO_3$, washed with water, ethanol and reprecipitated from DMF into methanol. An elemental analysis of PFSN gives a content of nitrogen from 15.0 to 15.5% (depending on a batch) which corresponds to $x = 0.9$ to 1.0. The yield was about 70%.

The instrumentation used for spectral measurements was the same as in our preceding paper (2). The photochemical behaviour was studied using high pressure mercury lamp (short wavelength radiation was cut-off with a glass filter, absorbed dose about 0.1 $J.s^{-1}\ cm^{-2}$).

All solution NMR spectra were recorded at 300.1 MHz for ^1H and 75.5 MHz for ^{13}C with deuterated dimethyl sulfoxide (DMSO-d_6) as solvent.

High-resolution solid-state ^{13}C NMR spectra were measured at 50.3 MHz using the standard combination of cross polarization (CP), dipolar decoupling (DD) and magic-angle spinning (MAS) (5). The MAS frequency was 4–5 kHz. Besides the conventional CP/MAS/DD spectra, also spectra with a delay of 40 μs without decoupling prior to acquisition were recorded. This experiment (sometimes called dipolar dephasing) provides spectra of carbons without directly bonded hydrogen (6).

Results and Discussion

4-Nitrophenylhydrazone of poly(4-formylstyrene) is soluble in DMF, DMSO or their mixtures with THF or acetone. It can be spin-cast from DMF solution on pre-heated substrates yielding films of good optical quality.

The polymer has T_g 230°C with onset at 213°C. As expected, T_g is very high not only because of the bulky substituents but also owing to dipole-dipole interactions. Wide-angle X-ray scattering (WAXS) measurements on a film obtained by evaporation of a DMF solution showed that the polymer is fully amorphous.

PFSN undergoes both photo and thermal crosslinking and bleaching in the solid state. These processes were followed similarly as in our preceding paper (2): Absorbances of the parent thin film (A_0), of the film after UV irradiation or heating (A_1) and of the same film after 1 min boiling in DMF/THF mixture (1 : 1 v/v) (A_2) were measured at the chromophore longest wavelength absorption (λ = 410 nm). The ratio A_1/A_0 shows the extent of the chromophore bleaching whereas ratio A_2/A_1 represents the measure of the extent of gelation (crosslinking). The UV-vis spectra of parent PFSN film and of the same film after 10 min heating at 250°C are shown in Figure 1.

Bleaching of PSFN caused by UV irradiation is shown in Figure 2. It was observed that films exhibiting $A_1/A_0 <$ ca 0.8 are fully gelled (the ratio A_2/A_1 is usually greater than unity for the completely gelled samples, probably because of a change in the film optical quality caused by extraction). The bleaching of films during heating is shown in Figure 3 (again, all samples with $A_1/A_0 <$ ca 0.8 are completely gelled). It is apparent that bleaching proceeds at a considerable rate even fairly below T_g. A comparison of curve for 150°C with curve 3 in Figure 2 in our preceding paper (2) (measured for the polymer with $x = 0.07$, in Figure 3 here see dashed curve) shows that the rate of bleaching is not dependent on the degree of substitution x. Also, the bleaching rate in poly(4-formylstyrene) only partially transformed to its 4-nitrophenylhydrazone ($x = 0.5$) is the same as in PFSN. Finally,

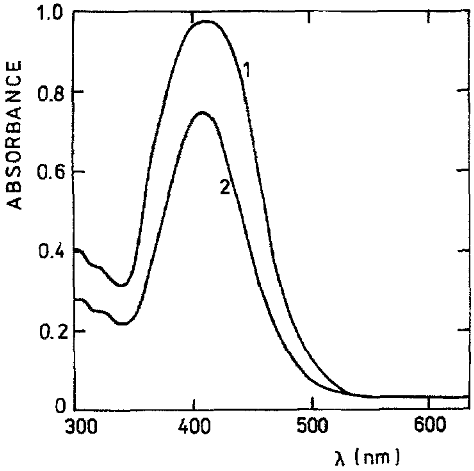


Figure 1: UV-vis spectra of PFSN thin films before (curve 1) and after (curve 2) 10 min heating at 250°C in air.

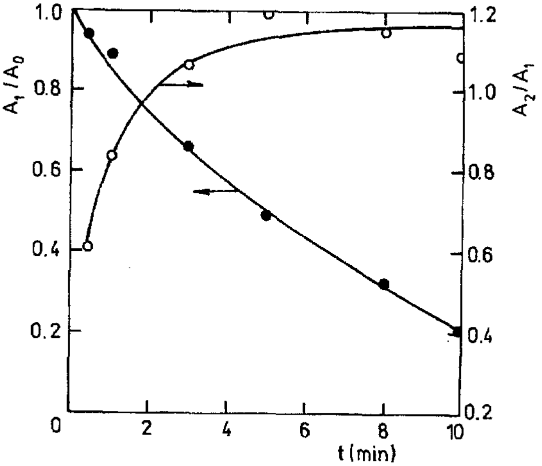


Figure 2: The extent of bleaching (A_1/A_0) and gelation (A_2/A_1) of PFSN during UV-irradiation in air (absorbed dose ca 0.1 J s^{-1} cm^{-2}).

the similar rate of chromophore decay was also observed with 4-nitrophenylhydrazone of poly[styrene-co-(4-formylstyrene)] (monomer ratio 1 : 2). Consequently, the bleaching is probably caused neither by a mutual reaction of two hydrazone groups nor by a reaction with reactive moieties such as residual carbonyl groups.

A pellet made from PSFN and pressed in a hydraulic press at 250°C for 5 min does not swell in DMF any longer. The sample is obviously very densely crosslinked. Swelling experiments on samples crosslinked at lower temperatures were not feasible because of the poor mechanical cohesion of the pellets.

We have tried to elucidate the nature of both thermal bleaching and crosslinking of PFSN. Thermogravimetric analysis (TGA) curve shows (Fig. 4) that the onset of

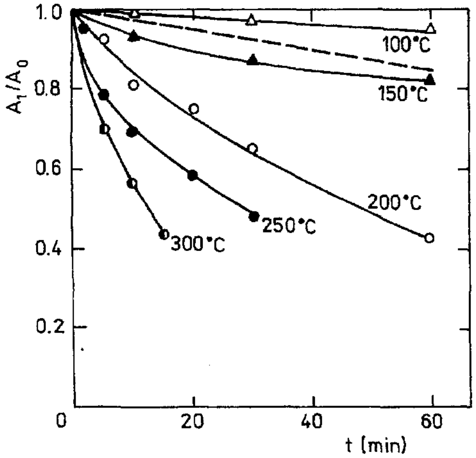


Figure 3: Bleaching of PFSN during heating in air. Dashed curve represents bleaching of the polymer with 7 mole % of 4-nitrophenylhydrazone groups at 137°C [cf. curve 3 in Fig. 2 in the previous paper (2)].

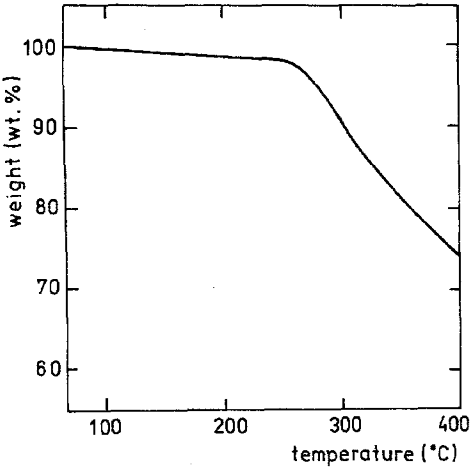


Figure 4: TGA curve for PFSN.

PFSN weight loss (degradation) is at 280°C. Therefore, we studied in more detail the fate of the sample heated in air at 250°C for 30 min during which a 50% drop in the chromophore absorbance was observed. After such treatment the polymer losses only about 1–3% of its weight. Consequently, the bleaching is not caused by splitting substituents into volatile fragments or the fragments immediately react with the polymer. As in our preceding paper (2), IR spectra show only some broadening of all bands during heating. NMR spectra, on the other hand, indicate substantial changes upon heating which are described in the following paragraphs.

As the PFSN is soluble e.g. in DMSO-d_6, the interpretation of its solid-state NMR spectrum was based on comparison with its solution ^{13}C NMR spectrum assigned by means of 1 D and 2 D ^{1}H and ^{13}C NMR spectra of PFSN, and on their relations to the spectra of poly(4-formylstyrene), benzaldehyde 4-nitrophenylhydrazone and 4-nitroaniline.

In the aromatic region, the ^{1}H NMR spectrum of PFSN exhibits four peaks; by means of the COSY spectrum those at 6.5 and 7.0 ppm are assigned to one aromatic ring, and those at 6.7 and 7.9 ppm to the other ring. The last named peak is overlapped by the signal of the –CH=N– group. The peaks at 6.5 and 7.0 ppm are broader, which might be caused by their greater sensitivity to steric structure of the backbone. This suggests their assignment to ring A. The ^{13}C NMR spectrum of PFSN in DMSO-d_6 solution is shown in Figure 5. The band assignment is based on a ^{1}H-^{13}C HETCOR spectrum and is in agreement with the published ^{13}C NMR spectrum of 4-nitroaniline (7). The lines at lowest and highest fields correspond to the carbons of ring B; the signal of the –CH=N– carbon lies at 142 ppm.

Solid-state ^{13}C NMR spectra of sample (PFSN) before and after heating are given in Figure 6. Only aromatic region is shown, as in the aliphatic region practically no changes could be observed on heating. The assignment of the peaks in the solid-state spectra is based on the high-resolution assignment. The spectra clearly show that

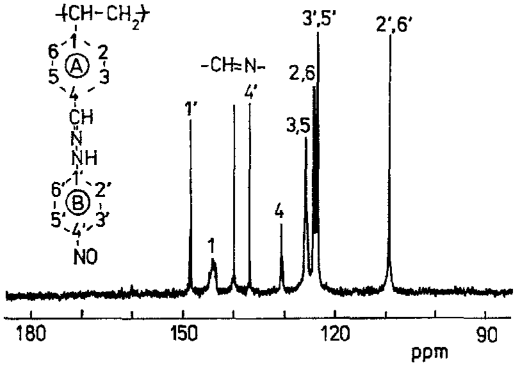


Figure 5: ^{13}C NMR spectrum of PFSN in DMSO-d_6 solution at 100°C.

large structural changes take place in the sample. In the spectra of quaternary carbons (c, d) we see that the lines assigned to carbons 4, 4′ and 1′ disappear after heating and the line assigned to carbon 1 only persists. A new line appears at ~ 165 ppm; also, a very broad line in the range 120–160 pmm is apparent. Conventional CP/MAS/DD spectra (a, b) display similar changes, although less discernible; moreover the line assigned to carbons 2′,6′ almost completely disappears after reaction.

From these changes observed in solid-state ^{13}C NMR spectra we may draw the following conclusions. The polystyrene-like backbone remains unchanged with the exception of the carbon 4 where changes of the substituents probably occur. The rest of the pendant group seems to undergo profound changes. However, it is difficult to interpret the spectra of the heated sample in terms of detailed chemical structure. The broad line in the range 120–160 pmm (d) suggests that a complex system of conjugated carbons without directly bonded hydrogen appears after heating. A question remains, however, why the formation of this system is not indicated by new bands in UV-vis

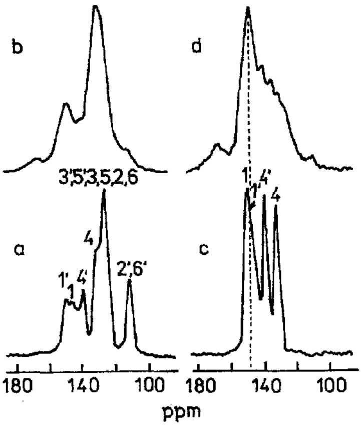


Figure 6: High-resolution solid state ^{13}C NMR spectra of PFSN before (a, c) and after (b, d) heating for 30 min at 250°C in air, measured with conventional CP/MAS/DD sequence (a, b) and with dipolar dephasing delay of 40 μs (c, d).

spectra. The new line at ~ 165 ppm is namely in the range typical of carboxyl, ester or amide carbonyl carbons on aromatic ring.

Conclusions

PFSN possesses some properties suitable for NLO application: the content of NLO chromophores is very high, the polymer is amorphous and has a high T_g, and it crosslinks to a large extent upon heating near T_g. The rate of crosslinking, which is perhaps too high for poling experiments, might be probably controlled, e.g., by varying the substitution degree of the polymer. The rapid chromophore decay, however, precludes practical use in nonlinear optics. Preliminary experiments showed, however, that this material could be used as a photoresist owing to its rapid bleaching and crosslinking during irradiation.

The bleaching of the thermal origin (not oxidative or hydrolytic) was observed also in NBPE (3). The chromophore bleaching can be fitted to an exponential rate law both in NBPE and PFSN. Probably, a slow chromophore decay is accompanied by a well-known, more rapid thermal syn – anti isomerization of the hydrazone group (8), which can cause (at most) 20% decrease in absorbance. It seems from comparison of data obtained at 150°C that the hydrazone chromophore in NBPE is at least one order of magnitude more stable than in PFSN. The main reason for this difference might be the fact that NBPE contains hydrazones of benzophenone moieties whereas PFSN those of benzaldehyde type. Therefore, we are turning our further attention to the possibilities of thermal stabilization of the polymeric 4-nitrophenylhydrazones by their chemical modification. The results of our effort in this direction will be described in our forthcoming paper.

Acknowledgement

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