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4-Nitrophenylhydrazones of partially formylated polystyrene, their properties and crosslinking

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Summary

The title polymers were prepared as potential non-linear optical materials with a degree of substitution 3–13 mole %. During UV-irradiation and/or heating near the glass transition temperature these polymers crosslink through the hydrazone groups and their UV-vis absorption band diminishes. Degrees of crosslinking of swollen samples were estimated. A possibility of simultaneous crosslinking and poling of these polymers is discussed.

Introduction

One of the most promising technologies for the preparation of the non-centrosymmetric nonlinear optical (NLO) materials for the second-harmonic generation (SHG) is the so-called poling of polymers. In this method, the polymer containing NLO – active chromophores (with high dipole moment and high hyperpolarizability) is heated near its glass transition temperature, T_g, and an electrical field is applied. An orientation of the NLO chromophores achieved in this way can be frozen-in (polymer system is poled) if the temperature is subsequently lowered well below T_g with the poling field still on (1).

Polymers with covalently bound NLO chromophores offer considerable advantages in comparison with mere polymer/chromophore blends (1): they can exhibit much higher densities of the chromophores without segregation and opacity; they are able to withstand much higher poling fields; they show higher SHG performance; after poling, the reorientation of chromophores to their random positions is slowed down. Nevertheless, this reorientation still represents a serious problem for the practical use of the poled polymers in most cases. One of the best ways of suppressing this process is to crosslink the polymer during poling (1).

Another important way of preparing non-centrosymmetric polymer systems required for SHG applications is a Langmuir-Blodgett (LB) technique (1) since polar NLO chromophores frequently tend to make contact with water phase and remain oriented during mono- or multilayer preparation.

During our investigation of partially formylated poly(methyl–phenylsilylene) (2) we revealed that 4-nitroanil and 2,4-dinitrophenylhydrazone of this material photocrosslink in the solid state when irradiated in the UV or near visible region and simultaneously heated near T_g. It is known (3) that nitroanils and nitrophenylhydrazones show high dipole moments (about 7.2 D) and high differences of dipole moments between excited and ground states (a measure of which is a solvatochromic shift of the longest wavelength absorption maximum between methanol and cyclohexane). We realized, therefore, that poly(silylenes) with these substituents should be capable of simultaneous poling and convenient crosslinking, thus fulfilling the requirements for the good SHG material. Moreover, 2,4-dinitrophenylhydrazone (and also 2-hydroxy-4-nitroanil) of partially formylated poly(methyl–phenylsilylene) easily forms LB multilayers with good

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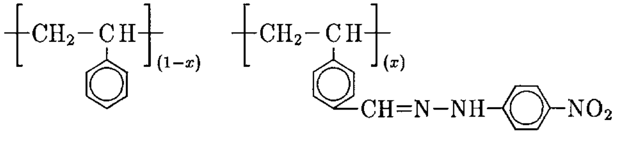
homogeneity (electrical properties of even a single monolayer of this material were successfully measured) (4). The polymers of this type seem to be interesting for both poling and LB technology.

In order to elucidate if the silyl radicals formed during irradiation of these poly(silylenes) (2) are responsible for this photocrosslinking we prepared a model material: 2,4-dinitrophenylhydrazone of partially formylated polystyrene (PS). We observed that this polymer also photocrosslinks and undergoes also thermal crosslinking. In addition, we prepared the 4-nitrophenylhydrazone derivative (denoted further as PSN) with a following formula



which should have a higher dipole moment than the 2,4-dinitrophenylhydrazone and which shows similar crosslinking. Both these polystyrene derivatives are more stable than the poly(silylenes) mentioned above and are very easy to prepare. They are, therefore, more suitable for detailed studies and potential applications than poly(silylenes) mentioned above. This communication deals with properties and photo- and/or thermal crosslinking of 4-nitrophenylhydrazone of partially formylated polystyrene (PSN).

Experimental

The partially formylated PS was prepared according to the published procedure (6) by the reaction of the parent polymer ($M_n = 150000$, $M_w/M_n = 1.92$) with $Cl_2CHOCH_3/SnCl_4$ in methylene chloride and subsequent hydrolysis. Three materials were obtained with the degree of substitution $x = 0.03$, 0.07 and 0.13. A crosslinked portion of the crude product (see Results and Discussion) was removed by filtration or centrifugation and the soluble polymer was twice reprecipitated from tetrahydrofuran (THF) solution with methanol.

The 4-nitrophenylhydrazones were synthesized as follows: To the boiling solution of 3 g of the formylated polystyrene in 400 ml THF, 2 g of 4-nitrophenylhydrazine dissolved in 100 ml of ethanol/hydrochloric acid mixture (4:1 by vol.) was slowly added. The mixture was boiled for 30 min and ca. 200 ml of THF was then distilled off. After that, the crude product was precipitated with methanol, twice reprecipitated (THF/methanol) and dried. The yield of the product (yellow powder) was about 60% of the theoretical.

High pressure mercury lamps were used for the study of the polymer photocrosslinking. The short wavelength part of UV light was always cut-off with a glass filter. The output energy of these sources was measured with wattmeter PS−V−103, Gentec. UV-vis spectra were recorded with an HP 8451 A (Hewlett-Packard) spectrometer. The IR spectra were measured with a Perkin-Elmer 577 apparatus. Wide-angle X-ray scattering (WAXS) experiments were performed with an HZG 4 spectrograph. The differential scanning calorimetry (DSC) curves were obtained using a Perkin-Elmer DSC 7 apparatus. The size exclusion chromatography (SEC) traces were recorded using PL−MIXED filled columns and THF as eluent; a calibration with PS standards was used for calculations of the molecular weightes. The stress-strain dependence on swollen crosslinked samples was measured using an apparatus described earlier (5).

The methods of determination of the extent of crosslinking reactions are described in detail in the following section.

Results and Discussion

Syntheses

It is generally required to keep a concentration of NLO-chromophores in a poled polymer as high as possible (1) (well above $x = 0.1$). Although it was reported (6) that the formylation of PS leads up to $x = 0.5$, our attempts to repeat these experiments were unsuccessful and polymers with $x > 0.13$ were completely crosslinked. It seems that for reaching high x, the use of starting material with much lower molecular weight or of another synthetic pathway is neccessary (6).

The syntheses of 4-nitrophenylhydrazones proceeded smoothly and without crosslinking. The high conversion of this reaction was easily checked with IR spectra: a strong band belonging to carbonyl group of formylated PS (around 1700 cm^{-1}) was completely missing in the products. The degree of substitution in these materials was determined using an elemental analysis: Polymers prepared contained 1.66, 2.23 and 4.27% N, which corresponds to $x = 0.03$, 0.07 and 0.13, respectively. These polymers are hereinafter denoted as PSN–03, PSN–07 and PSN–13.

M_n determined for PSN–07 was 143 000, $M_w/M_n = 2.42$. Although these data are not fully comparable with those of starting material, due to different solution properties of both polymers, it may be concluded that PS main chain suffers little (if any) damage during its chemical modification.

Properties

All PSN samples are soluble in THF, 1,4-dioxane and acetone. Those with higher x, however, only swell in another solvents typical for PS (aromatics and chlorinated solvents). They can be easily spin-casted from their solution, yielding films of a good quality. To our present knowledge, the polymer films are quite stable towards both acidic and basic media. Polymer solutions in THF turn from yellow to red-pink when the NaOH solution is added because of well-known hydrazone salt formation (7). PSN needs to be stored in the absence of light because of its photosensitivity.

The structure of PSN was investigated using WAXS measurements on about 0.3 mm thick films prepared by evaporation of its concentrated solution. Both PSN–07 and PSN–13 are amorphous, which is a sign that they might have good optical properties, desirable for SHG applications.

Both PSN-07 and PSN-13, together with starting PS were studied using DSC in the range 0–250°C. Only one exotherm (ΔH about 0.275 J/g) was always observed, which can be attributed to T_g as follows: PS: $T_g = 82.8$°C; PSN–07: $T_g = 120.4$°C; PSN–13: $T_g = 139.0$°C. It is apparent that the substitution has a considerable effect on T_g; the polymer main chain is probably quite stiffened by the attached large hydrazone groups.

Some spectral properties of PSN are discussed in the following section.

Crosslinking

As was already mentioned, PSN undergoes both photo- and thermal crosslinking in the solid state.

The primary stages of crosslinking are quite suitable for the evaluation of the crosslinking rate, since the molecular mobility of the system has not yet been changed significantly. These stages were investigated as follows: First, films with an absorbance from 0.2 to 0.4 at the longest wavelength of 4-nitrophenylhydrazone absorption (400 nm) were prepared by spin-coating on glass substrates. The UV-vis spectra of the film in the region 300–600 nm were measured (giving an initial absorbance at λ_{max}, A_o). After that, the film was irradiated and/or heated for the chosen period. Its UV-vis spectrum was remeasured (providing A_1). Subsequently, the film was immersed into the boiling THF for 1 min, and, after evaporation of the solvent, the spectrum was measured again, providing the A_2 value. The A_2/A_1 ratio gives an information on the insoluble (gelled) portion of polymer. The typical spectra of parent, irradiated and extracted material are shown in Fig. 1.

An initial experiment showed that crosslinking proceeds through the attached 4-nitrophenylhydrazone moieties: Whereas the sample of PSN–13 was almost completely

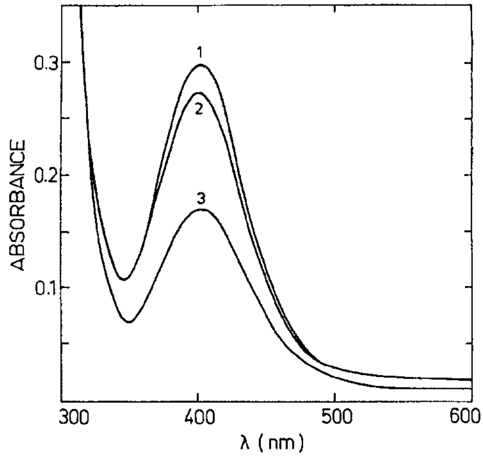


Figure 1: UV-vis spectra of PSN−13: curve 1 – parent film; curve 2 – after 10 min of irradiation (absorbed dose ca 0.01 $J.s^{-1}.cm^{-2}$); curve 3 – after extraction with boiling THF for 1 min

gelled after 30 min of irradiation, the similarly irradiated film of the PS with admixed 13 mole % of benzaldehyde 4-nitrophenylhydrazone (BN) was completely splashed from the substrate with boiling THF. When this blend was heated at the temperature suitable for the thermal crosslinking (157°C, 10 min), BN completely sublimed off, leaving fully soluble polymer.

The time dependence of A_1/A_0 during irradiation or heating near or above T_g (Fig. 2) shows that both thermal treatment and irradiation of PSN result in some decrease of the chromophore absorption. After a prolonged period there is also some blue shift of this band (5–30 nm). It is known that BN exists as a mixture of syn- and anti isomers and during irradiation (or heating) the syn → anti isomerization occurs (8), accompanied by a ca. 18 nm blue shift and 20% decrease in absorbance at λ_{max}. Consequently, this isomerization is partially responsible for the bleaching observed with PSN. After prolonged period, however, A_1/A_0 value drops to 0.1 (see below) and this effect cannot be attributed solely to the isomerization.

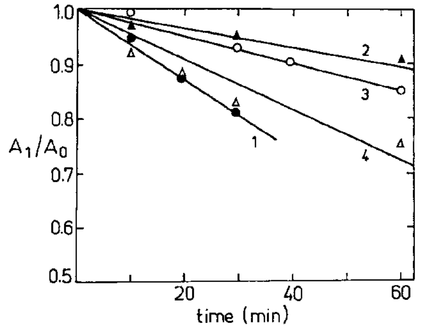


Figure 2: Time dependence of A_1/A_0 (extent of bleaching): curve 1 (●) PSN−07, irradiated at 25°C; curve 4 (△) PSN−13, irradiated at 25°C (absorbed doses 0.01 $J.s^{-1}.cm^{-2}$); curve 2 (△) PSN−07, 107°C in dark; curve 3 (○) PSN−07, 137°C in dark

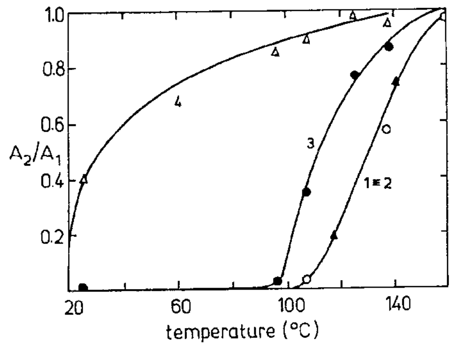


Figure 3: A_2/A_1 (extent of gelation) at given temperatures: curve 1 (○) PSN−07, 10 min heated in dark; curve 3 (●) PSN−07, 30 min heated in dark; curve 2 (△) PSN−13, 10 min heated in dark; curve 4 (△) PSN−07, 10 min heated and irradiated (absorbed dose 0.01 $J.s^{-1}.cm^{-2}$)

It can be seen in Fig. 3 (curves 1, 2, 3) that the thermal crosslinking proceeds significantly only at temperatures near or above T_g, with similar rates for both PSN−07 and PSN−13. Time dependence of gel formation for purely thermal crosslinking is shown in Fig. 4, curve 2. The photocrosslinking, on the other hand, takes place even at room temperature, although its rate is increased with increasing temperature (Fig. 3, curve 4 and Fig. 4, curves 1, 3).

It may be expected that the bleaching of polymers during treatment is somehow connected with the crosslinking reaction. To check this assumption, A_2/A_1 values (the extent of gelation) are plotted vs. $(1 - A_1/A_0)$ values (the extent of bleaching) in Fig. 5. Although the data scattering is considerable, both values show a linear correlation. It seems that the thermal bleaching is accompanied with more extensive gelation than the photochemical one.

Attempts were made to follow the chemical changes during extensive chromophore absorption bleaching using IR spectroscopy. The initial IR spectrum of the PSN−13 film on a KBr pellet shows some bands characteristic for hydrazone moiety (1595 cm^{-1} belonging to azomethine group, 1300, 1270 and 1105 cm^{-1}). Spectra were measured again after prolonged illumination or heating. However, even after 3 h of irradiation or heating at 180°C for 30 min, all bands in the IR spectrum show only about half intensity , which may be attributed to the increasing opacity of the sample in IR region. On the other hand, the chromophore absorption band at 400 nm in the films on glass almost disappeared after the same treatment ($A_1/A_0 = 0.15$). It should be noted, however, that an azomethine vibration band at 1595 cm^{-1} is superimposed over a strong band belonging to PS at

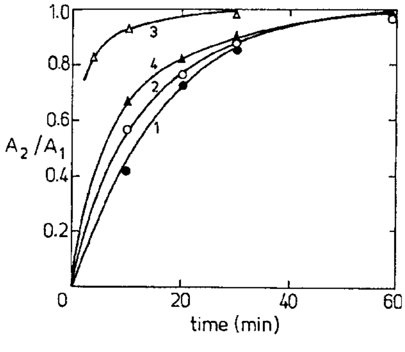


Figure 4: Time dependence of A_2/A_1 (extent of gelation): curve 4 (△) PSN−13, irradiated at 25°C; curve 1 (●) PSN−07, irradiated at 25°C; curve 3 (△) PSN−07, irradiated and heated at 137°C (absorbed doses 0.01 $J.s^{-1}.cm^{-2}$); curve 2 (○) PSN−07, 137°C in dark

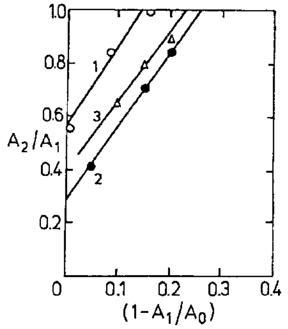


Figure 5: A_2/A_1 (extent of gelation) plotted vs. $(1 - A_1/A_0)$ (extent of bleaching): curve 2 (●) PSN−07, irradiated at 25°C; curve 3 (△) PSN−13, irradiated at 25°C (absorbed dose 0.01 $J.s^{-1}.cm^{-2}$); curve 1 (○) PSN−07, 137°C in dark

1605 cm^{-1} in PSN and the changes in its intensity can be probably hardly followed if the molar concentration of hydrazone in PSN−13 is only about 13%. In order to make the potential chemical changes on hydrazone group more apparent the films prepared from a blend of PS with BN (1:1 by weight) were also irradiated. Again, no chemical changes were visible in IR spectra, whereas UV-vis spectrum exhibited an extensive bleaching.

Since all experiments described above were performed in the presence of air, we had to check if oxygen plays a role during bleaching and/or crosslinking processes. Therefore, we evacuated a film of PSN−13 at 10^{-4} Pa for three days (to remove sorbed gases) and then the sample was irradiated for 30 min at room temperature in vacuo. The A_1/A_0 ratio was 0.91 for this sample and the A_2/A_1 value was 0.41. Both the extent of bleaching and gelation are lower than in the presence of air (see Figs 2 and 4). Although some influence of oxygen cannot be excluded in this way since this gas might be sorbed or even chemisorbed very firmly to the polymer, it can be judged that oxygen would promote both processes.

ESR spectrum of the solution of PSN−07 in benzene was also recorded before and during UV-illumination. No radicals were detected which may indicate that the bleaching/crosslinking are not processes involving radicals.

Consequently, our knowledge about the mechanism of both bleaching and crosslinking remains poor. We expect that crosslinking proceeds via reactions of azomethine groups. Hydrazones of aldehydes are generally thermally stable substances. During prolonged heating, however, the compounds with azomethine groups undergo condensation or addition reactions (9) which may lead to the formation of partially or fully saturated nitrogen containing heterocycles. Some photoinduced decay is reported to proceed also during the irradiation of BN (8). These reactions might interrupt the conjugation in the chromophore resulting in lower and blue-shifted absorption (bleaching) or even in formation of new bands in UV-vis spectra. Whereas the first effect was always observed during-crosslinking, no new bands were detected in the 200–300 nm region after 30 min of irradiation (measured on PSN−13 sample cast on quartz slide).

Although the measurements of polymer gelation described above give some data on relative rates of crosslinking, they do not provide us with any information on the crosslinking extent. Such knowledge is of some importance since it is probable that the potential NLO activity of hydrazone groups participating in crosslinking is substantially changed. One can also expect, that the roughly anti parallel arrangement of two reacting groups is required during crosslinking which leads to the low dipole moment of the resulting moiety. In order to estimate the crosslinking degree, we performed some experiments on swelling of the highly crosslinked PSN−13 in THF. For irradiation, a stronger light source was used in this case with about 11 times higher output than that used above.

In the thermal crosslinking, the pellet of tested polymer PSN−13 (0.5 mm thick) was pressed in a hydraulic press at 160°C for a chosen period . Then, it was swollen in THF for 24 h and the volume fraction ϕ_p of the polymer in swollen sample was determined (see Table 1, samples 1, 2, 3).

In the case of photocrosslinking, the situation is naturally complicated by the low penetration depth of light in these highly absorbing materials (ε is about 40 l.cm^{-1}.g^{-1} for PSN−13 at 400 nm). Therefore, the following procedure was developed: A spot of the polymer was formed by careful dropping its dilute THF solution onto a clean mercury surface. The absorbance of the dried polymer layer at the main mercury lamp emission wavelength (366 nm) was around 1.0. This, together with a fact that some light is reflected back to the film from the mercury surface, ensures a quite homogeneous irradiation of the sample. After irradiation, the mercury was covered with THF. Since the polymer film easily slides on the mercury surface the polymer spot rapidly swelled to its equilibrium dimensions which were measured. The increase in the spot diameter (R_{st}/R_{pt}) as well as the corresponding volume fraction ϕ_{pt} of polymer in swollen sample (provided that the polymer swelling is isotropic) is listed in Table 1 (samples 5, 6, 7).

The spot of PSN−13 on mercury was also thermally crosslinked for 15 min at 160°C in the dark (sample 4, Table 1). This spot when swollen in THF increased its diameter from 16 to 23 mm which corresponds to ϕ_{pt} value of 0.333. The bulk sample after the same thermal treatment increased its volume after swelling 30 times, i.e. $\phi_p = 0.0333$. Although the difference between swelling measured by both methods is large, it might be assumed that there is a roughly linear correlation between volume increase determined in both ways. Using this assumption the data from thin film swelling were recalculated to the corresponding swelling in bulk, V_s/V_p (see Table 1).

Data obtained from swelling experiments were treated as follows (10): modulus at equilibrium $G_e = 1.5 \times 10^3$ Pa was determined for swollen sample 1. It is known that $G_e =$

Table 1: Crosslinking of 4-nitrophenylhydrazone of partially formylated polystyrene (PSN-13) and its swelling in THF

Sample[a]	Crosslinking conditions			R_{st}/R_{pt}[c]	ϕ_{pt}[d]	ϕ_p[e]	$\nu_e.10^6$[f]
	time (min)	temp (°C)	light[b]				(mol.cm^{-3})
1	15	160	off	–	–	0.0333	3.8
2	60	160	off	–	–	0.0658	15.8
3	120	160	off	–	–	0.0793	18.2
4	15	160	off	1.44	0.333	0.0333	3.8
5	5	25	on	1.59	0.25	0.0250	2.3
6	10	25	on	1.25	0.50	0.0500	7.9
7	15	25	on	1.15	0.666	0.0666	13.7

[a] Samples 1–3 swollen in bulk, samples 4–7 swollen as thin films, see the text for details

[b] Absorbed dose ca. 0.11 J.s^{-1}.cm^{-2}

[c] Increase in polymer spot diameter caused by swelling

[d] Volume fraction of polymer in swollen sample corresponding to the spot diameter increase

[e] Volume fraction of polymer in swollen sample

[f] Concentration of elastically active chains in crosslinked polymer

$RT\nu_e A(r_d^2/r_0^2)\phi_p^{1/3}$, where ν_e is a concentration of elastically active chains in mol.cm^{-3}. $A = 0.5$ for the phantom network with tetrafunctional crosslinks and r_d^2/r_0^2 is close to unity for networks formed in the solid state, therefore $\nu_e = 3.84 \times 10^{-6}$ mol.cm^{-3}. The interaction parameter χ was then calculated: $\chi = [-\nu_e V_s A - \ln(1-\nu_e)]/\phi_p^2 - \phi_p^{-1} = 0.368$ (V_s is molar volume of the solvent, 81.38 cm^3.ml.mol^{-1} for THF). It should be noted that this value represents a rough approximation since the Gaussian distribution of the chain lengths is no more valid for such highly swollen sample and parameter χ is generally concentration-dependent. The ν_e values (listed in Tab. 1) can be calculated following Flory's equation for the network with tetrafunctional crosslinks:

$$\nu_e = -\rho_p[\phi_p + \chi\phi_p^2 + \ln(1-\phi_p)]/[2.V_s\rho_s(\phi_p^{1/3} - \phi_p/2)]$$

where ρ_s and ρ_p are densities of solvent and polymer, respectively (0.889 g.cm^{-3} for THF and 1.08 g.cm^{-3} for PS).

Although the precision of listed ν_e values is very limited they still provide us with some data on the crosslinking degree. For example, the value $\nu_e = 13.7 \times 10^{-6}$ mol.cm^{-3} for irradiated sample 7 corresponds to average molecular weight of the polymer between crosslinks $M_c = 2/(\nu_e.\rho_p) = 39000$, i.e., ca. 4 crosslinks are present in one polymer chain. Since the chromophore absorption band almost completely disappears after such treatment ($A_1/A_0 = 0.1$) one can judge that most of the ca. 100 hydrazone groups originally bound on one polymer chain are already consumed in bleaching whereas about 4 of them participate also on crosslinks. We do not know, however, whether the crosslinking is preceded by bleaching or these two processes are competitive.

It can be summarized that the bleaching is a sign that chromophore suffers a considerable damage during crosslinking. Since it is necessary to keep chromophore concentration as high as possible for SHG applications of poled films, it is desirable to find poling conditions where damage on NLO active groups is still low and crosslinking proceeds to an extent sufficient for the stabilization of the poled system.

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