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Published in:
Macromolecules

DOI:
10.1021/ma951202w

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1996

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Download date: 03-01-2019
Second-Harmonic Generation from Floating Monolayers and Langmuir–Blodgett Multilayers of Poly(isocyanide)s

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Received August 17, 1995; Revised Manuscript Received April 25, 1996

ABSTRACT: Floating monolayers as well as Langmuir–Blodgett (LB) films of poly(isocyanide)s containing NLO-active side chains appear to be capable of generating second-harmonic light. Spin-coated films and cast films of these polymers do not show this behavior. These results indicate that the NLO activity of the LB films originates from the orientation of the side chains obtained at the air–water interface. In the case of poly(isocyanide)s with relatively hydrophobic side chains the second-harmonic intensities generated from the LB films are small, probably because the films are of the Y-type. Poly(isocyanide)s with more hydrophilic side chains form LB films which are Z-type. These films show stable second-harmonic generation without the need of poling with high electrical fields at high temperatures.

Experimental Section

Materials. The route which was used to synthesize the different polymers is given in Scheme 1. Together with Table 1, Scheme 1 shows which precursors and polymers were synthesized and investigated in this study.

Synthesis. The general procedures have been outlined elsewhere. A detailed description of the procedures is available on request in the supporting information.

NLO Measurements. The NLO activity of floating Langmuir–Blodgett layers was determined by measuring the generated second-harmonic intensity using the setup described by Sheeren et al. and using silver as a reference.9 The NLO activity of LB films was determined by measuring the second-harmonic intensity generated from multilayered samples on glass substrates, using the setup described by Chossen et al.10 The second-harmonic intensity was referenced to a clean silver mirror (100% reflectance) with \( \chi^{(2)} = 1.3 \times 10^{-10} \) esu (at \( \lambda \)) and \( \chi^{(2)} = 10^{-10} \) esu (at \( \lambda \)), respectively. For conversion into SI units one can use, in the case of \( \beta \), the relationship 1 cmV\(^{-2}\) = 2.7 × 10\(^{-16}\) esu and, in the case of \( \chi^{(2)} \), 1 CV\(^{-2}\) = 2.7 × 10\(^{14}\) esu.

Results and Discussion

In our experiments the square root of the second-harmonic intensity was plotted as a function of the number of layers \( n \). In the case of optically transparent films with thicknesses less than \( \lambda \), one expects a linear relationship between the two variables, as shown in eq 1. However, in the case of films which...
of the floating monolayer, it was assumed that the monolayer thicknesses of butyrate are compiled in Table 2. For the calculations of

Second-Harmonic Generation from Poly(isocyanide)s

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Table 2. Second-Order Susceptibilities of Monolayers of Polymers 8 and 9 and Mixed Monolayers of 10 and AB

<table>
<thead>
<tr>
<th>polymer</th>
<th>mole fraction of poly(isocyanide)</th>
<th>π (\text{mN/m})</th>
<th>(\chi_{zzz}) (10⁻⁹ esu)</th>
<th>(\chi_{zzz}) (10⁻⁹ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1.00</td>
<td>10</td>
<td>5.5</td>
<td>22.0</td>
</tr>
<tr>
<td>9</td>
<td>1.00</td>
<td>10</td>
<td>7.4</td>
<td>27.7</td>
</tr>
<tr>
<td>10/AB</td>
<td>0.28</td>
<td>15</td>
<td>8.1</td>
<td>34.1</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>15</td>
<td>9.8</td>
<td>31.1</td>
</tr>
<tr>
<td></td>
<td>0.66</td>
<td>15</td>
<td>10.0</td>
<td>37.7</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>15</td>
<td>9.5</td>
<td>44.6</td>
</tr>
</tbody>
</table>

...}

NLO Properties of Poly(isocyanide)s with Hydrophobic Side Chains. Floating Monolayers.

...}

Table 1. Polymers and Their Precursors Used in This Study

<table>
<thead>
<tr>
<th>compd</th>
<th>R</th>
<th>R'</th>
<th>config at C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a–d</td>
<td>N(C₄H₉)₂</td>
<td>H</td>
<td>R,S</td>
</tr>
<tr>
<td>9a–d</td>
<td>N(C₄H₉)₂</td>
<td>H</td>
<td>S</td>
</tr>
<tr>
<td>10a–d</td>
<td>N(C₄H₉)₂</td>
<td>NO₂</td>
<td>S</td>
</tr>
<tr>
<td>11a–d</td>
<td>morpholine</td>
<td>NO₂</td>
<td>S</td>
</tr>
<tr>
<td>12a–d</td>
<td>morpholine</td>
<td>NO₂</td>
<td>R,S</td>
</tr>
</tbody>
</table>

...}

display absorption at the doubled frequency, i.e., at \(\lambda = 532\) nm, the second-harmonic intensity \(I_{2\omega}\) generated by the film is diminished because of absorption occurring in the film itself. The expression for the generated second-harmonic light in that case has to be changed, i.e., in such a way that it includes the absorption factor \(I = I_0 \times 10^{-dn}\), where \(\epsilon, d, n\) denote the extinction coefficient, thickness of one layer, and number of layers, respectively (eq 2).

\[
\sqrt{I_{2\omega}} = \text{Cn} \quad \text{(1)}
\]

\[
\sqrt{I_{2\omega}} = (\text{Cn}) \times 10^{-dn/2} \quad \text{(2)}
\]

The obtained curves were fitted to the function given by eq 2, and the fitting parameter, C, was used to calculate the different values of the \(\chi^{(2)}\) tensor, viz., \(\chi_{zzz}\), \(\chi_{xxz}\), and \(\chi_{zzz}\).

NLO Properties of Poly(isocyanide)s with Hydrophobic Side Chains. Floating Monolayers. Second-harmonic generation (SHG) measurements were carried out approximately 15 min after the desired surface pressure had been reached and the film area had become constant. Second-order susceptibilities were calculated from the experimental data using the procedure of Dick et al., neglecting the refractive index of the floating monolayer, i.e., \(n_{\text{film}} = n_{\text{water}} = 1.32\).

The results of the measurements of the second-harmonic generation on floating monolayers of polymers 8 and 9 and mixed monolayers of 10 and AB (amylose butyrate) are compiled in Table 2. For the calculations it was assumed that the monolayer thicknesses of polymers 8 and 9 were the same as those of polymer 10, i.e., 2.73 nm. The fact that the nitro group which is present in polymer 10 is completely buried within the side chains makes this assumption valid.

The \(\chi_{xxz}\) and \(\chi_{zzz}\) values of polymer 9 measured at \(\pi = 10\) mN/m were slightly higher than those of polymer 8. One might conclude from this result that a poly(isocyanide) prepared from an optically pure monomer (polymer 9) gives rise to an enhancement of the second-harmonic signal. One should, however, take into account that the error in the experiments is approximately 25%. In other words: One may not conclude from these measurements that polymer 9 adopts a more non-centrosymmetrical structure at the air–water interface than the racemic polymer 8.

At a surface pressure of 15 mN/m, polymer 9 displayed nearly the same \(\chi^{(2)}\) values as at a surface pressure of 10 mN/m. For a well-behaved monolayer, with all side chains located at the air–water interface, one would expect that the \(\chi^{(2)}\) values become larger at higher surface pressure, simply because in the latter case more chromophores are present per unit area. Probably the monolayer of 9 is pushed into thicker domains in which the chromophores adopt a random orientation. At a low surface pressure these domains are smaller and less numerous than at a higher surface pressure. This explanation would be in agreement with the morphology of the floating film, as revealed by electron microscopy for the comparable polymer 10.

For the mixed monolayer of polymer 10 and AB, \(\chi_{zzz}\) increased with increasing amount of 10 in the film (Table 2). The increase was, however, smaller than expected for polymers that are completely located at the air–water interface. As was shown earlier by us,\(^{12}\) not all segments of polymer 10 are situated at the interface, which may explain why the increase is relatively small. Changing the surface pressure from 15 mN/m to 25 mN/m gave rise to higher \(\chi^{(2)}\) values. The floating layer composed of 66% polymer 10 showed lower \(\chi^{(2)}\) values than the layer composed of 28% polymer 10. This result can be explained only if we assume that the former layer contains regions in which the chromophores have a random orientation. Such regions may arise if the floating layer forms thick fluid-like droplets or when it is in a collapsed state.

LB Multilayers. The NLO activities of films of polymers 8 and 9 and mixed films of 10 and AB were determined by measuring the second-harmonic intensity generated by multilayered samples on glass substrates. Poly(isocyanides) prepared from racemic mixtures of monomers are not expected to generate any second-harmonic signal. Nevertheless, they displayed a small second-harmonic signal, which may be the result of irregularities during the transfer. The LB films probably were not perfectly Y-type and, as a consequence, did not have a perfect centrosymmetrical struc-
The NLO activities of LB multilayers prepared from poly(isocyanide)s with relatively hydrophobic side chains exhibit little second-harmonic generation, probably because the orientation of the chromophores in adjacent layers of the multilayered film is antiparallel. The latter is the result of a quasi-Y-type deposition process.

In the floating monolayers the \( \chi^{(2)} \) values of polymer 12 are approximately 2 times higher than those of polymer 11. In the case of the LB multilayers the \( \chi^{(2)} \) values match. We explain this from the fact that the orientation of the side chains of polymer 12 in the floating monolayer is slightly more perpendicular to the surface than in the LB film. The extra orientation of the chromophores obtained from the interaction with the water surface is reduced in the LB film where this interaction is lacking. The possible orientations of the side chains of 12 in the different situations are schematically depicted in Figure 2.

**Conclusions**

In this study we have shown that rigid-rod polymers substituted with NLO-active chromophores can be successfully applied as building blocks to construct second-order NLO materials with enhanced time- and temperature stability of the polar order. In the following we will summarize the most important results of our study.

Contrary to expectation, floating monolayers of the poly(isocyanide)s do not display enhancement of the second-harmonic signal when the polymer is optically active.

LB multilayers prepared from poly(isocyanide)s with relatively hydrophobic side chains exhibit little second-harmonic generation, probably because the orientation of the chromophores in adjacent layers of the multilayered film is antiparallel. The latter is the result of a quasi-Y-type deposition process.

It has been possible to prepare thick LB films from poly(isocyanide)s with NLO-active side chains, which display a preferred orientation of the chromophoric groups. This preferred orientation is obtained at the water interface, is characteristic for the generation of the second-harmonic signal. As a correct reference sample for this situation, we were not able to calculate the different components of the \( \chi^{(2)} \) tensor.

**NLO Properties of Poly(isocyanide)s with Hydrophilic Side Chains. Floating Monolayers.** Measurements were performed on polymers 11 and 12 as described in the previous section, and the data are presented in Table 3. Polymer 12 shows higher second-order susceptibilities than polymer 11, which is understandable because its side chains can have a more parallel orientation than those of the latter polymer. Probably because of the presence of two ester groups per side chain, polymer 11 occupies more space, resulting in a quasi-antiparallel alignment of the chromophores and as a consequence a lower SHG (Figure 1).

It appears that \( \chi_{xxz} \) is higher than \( \chi_{zxx} \) in all cases and that the ratio \( \chi_{xxz}/\chi_{zxx} \) is even larger in the case of polymer 11 compared to polymer 12. The chromophores in polymer 11 probably have a more parallel orientation with respect to the air–water interface than those in polymer 12.

Also the distribution of the side chain orientations may be different for the two polymers. Because the chromophores are covalently bound to a rigid polymer backbone, it is useless to calculate their average angle of inclination. They will be restricted in their movements, and some of them will be forced to have orientations that are different from those of other groups.

**LB Multilayers.** The NLO activities of LB multilayers of mixtures of polymers 11 and 12 with 5 were determined on samples deposited on glass substrates. The samples consisted of 6–100 layers of polymer mixtures. The films were found to absorb light at 532 nm, and the second-harmonic intensity was therefore calculated in the same way as described in the previous section. The results are compiled in Table 4.

![Figure 1](image1.png) **Figure 1.** Schematic representation of the orientations of the side chains of polymers (A) 11 and (B) 12 in the LB film. One helical turn is shown.

![Figure 2](image2.png) **Figure 2.** Schematic representation of the orientations of the side chains of polymer 12 in (A) monolayers and (B) LB films.

| Table 3. Second-Order Susceptibilities of Floating Monolayers of Polymers 11 and 12 |
|-------------------|---------|---------|---------|---------|
| polymer | \( \chi^{(2)} \) (mN/m) | \( \chi_{zzz} \) (10\(^{-9}\) esu) | \( \chi_{zzz} \) (10\(^{-9}\) esu) | \( \chi_{zzz} \) (10\(^{-9}\) esu) |
| 11 | 1 | 5.5 | 1.4 | 27.0 |
| 5 | 5.7 | 1.4 | 32.2 |
| 15 | 7.2 | 0.7 | 43.7 |
| 12 | 1 | 10.5 | 5.2 | 46.8 |
| 5 | 17.9 | 4.8 | 59.9 |
| 15 | 14.8 | 1.9 | 87.1 |

| Table 4. Second-Order Susceptibilities of Mixed LB Films of Polymers 11 and 12 with Polymer 5 |
|-------------------|---------|---------|---------|---------|
| polymer | mole fraction of dye polymer | \( \chi_{xxz} \) (10\(^{-9}\) esu) | \( \chi_{zxx} \) (10\(^{-9}\) esu) | \( \chi_{zxx} \) (10\(^{-9}\) esu) |
| 11 | 0.23 | 3.7 | 1.3 | 13.5 |
| 0.44 | 5.1 | 2.2 | 22.3 |
| 0.15 | 1.9 | 0.8 | 7.5 |
| 0.37 | 4.6 | 1.9 | 18.5 |
| 0.56 | 7.0 | 2.9 | 27.9 |
air–water interface and is maintained in the multilayered film, leading to stable NLO activity. Our polymers with hydrophilic side chains possess an orientational stability which is unprecedented in nonpoled and non-cross-linked systems.

Supporting Information Available: Experimental details of the synthesis of the precursors and polymers used in this study (11 pages). Ordering information is given on any current masthead page.

References and Notes

(2) Williams, D. J. Polymers in nonlinear optics, Electronic and photonic applications of polymers; Bowden, M. J., Turner, R. S., Eds.; Advances in Chemistry 218; American Chemical Society: Washington, DC, 1988; p 297.