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Editor's Choice

Refractive Index Changes in Polymers Bearing Pendant Active Ester Groups by Thermal Rearrangement Reaction

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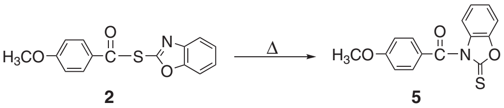
Linear and branched polymers bearing *S*-(2-benzoxazolyl) thioester groups were selectively synthesized by free radical and photoinitiated radical polymerization, respectively, of *S*-(2-benzoxazolyl)-4-vinylthiobenzoate. Upon heating, the pendant *S*-(2-benzoxazolyl) thioester groups were converted to 3-acylbenzoxazoline-2-thione groups, accompanied with a change of refractive index (Δn) of about $+0.01$ in both cases. The structural conversion was confirmed by UV–vis and IR spectroscopy, as well as comparison with authentic polymers bearing 3-acylbenzoxazoline-2-thione groups (similarly synthesized from 3-(4-vinylbenzoyl)benzoxazoline-2-thione). Application of such thermally induced rearrangement reactions may provide a new approach for obtaining materials whose refractive index can be changed by heat (e.g., generated by a laser beam).

Materials whose refractive index (n) can be tuned or modified are required for fabrication of optical waveguides, switches, and data storage devices,[1] and various UV-responsive functional polymers have been developed for such applications.[2] Kern et al. reported that exposure of thiocyanate-bearing polymer films to UV light resulted in isomerization of thiocyanate (–S–C≡N) to isothiocyanate (–N=C=S), accompanied with a refractive index change (Δn about $+0.03$).[3] Recently, photo-Fries rearrangement of aromatic ester[4] or *N*-phenylamide[5] moieties was also reported to result in a significant increase of polymer refractive index (up to $\Delta n = +0.1$). Nishikubo et al. prepared polymers with pendant bicyclo ortho ester groups and observed Δn values in the range between $+0.011$ and $+0.023$ after photoinitiated cationic curing of the polymers.[6] The refractive index change Δn is considered to be primarily due to the difference of molar refraction (R) of the functional groups before and after reaction, according to the Lorentz–Lorenz equation:[7]

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} = \frac{n^2 - 1}{n^2 + 2} \cdot V \qquad (1)$$

where M is the molecular weight ($M\,\mathrm{g\,mol^{-1}}$), n is the refractive index, ρ is the density, and V is the molecular volume.

To our knowledge, there are only a few reported examples of the use of heating to generate an increase of refractive index, i.e., it was reported that the heat-induced conformational change of poly(di-*n*-hexylsilane) from trans-planar to random helix was accompanied with a refractive index increase.[8] Also, it was reported that the thermal isomerization of quadricyclane (QC) to norbornadiene (NB) groups resulted in an increase of refractive index (this is the reverse reaction of the photoisomerization from NB to QC).[9] Since many heat-induced structural changes of organic molecules are known,[10,11] we considered that other such reactions might be available to generate refractive index changes. Here, we focused on the thermal rearrangement reaction of *S*-(2-benzoxazolyl) thioester (*S*-acyl) to 3-acylbenzoxazoline-2-thione (*N*-acyl).[12,13] The rearrangement generates a polar functional C=S bond, which is expected to cause an increase of the molar refraction R. Therefore, we speculated that thin films of polymer containing *S*-benzoxazolyl thioester moieties might show an increase of refractive index on exposure to heat. In this study, we designed and synthesized a styrene monomer bearing *S*-(2-benzoxazolyl) thioester moiety, and synthesized linear and branched polymers bearing *S*-(2-benzoxazolyl) thioester moieties by means of simple radical and photoinitiated radical polymerizations, respectively. We then examined the refractive index change of thin films of these polymers upon heating. We also examined whether the structural difference between the linear and branched polymers influenced the change of refractive index.

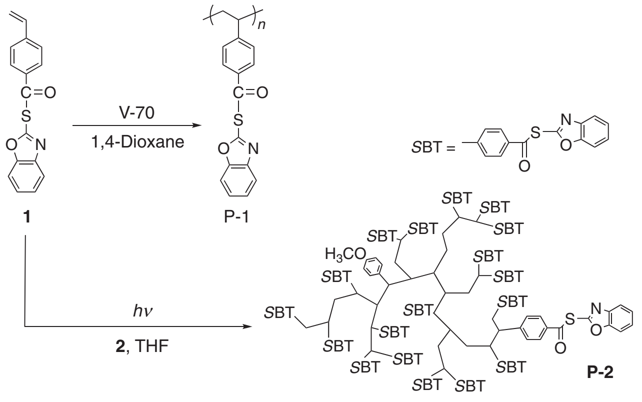


2 **5**

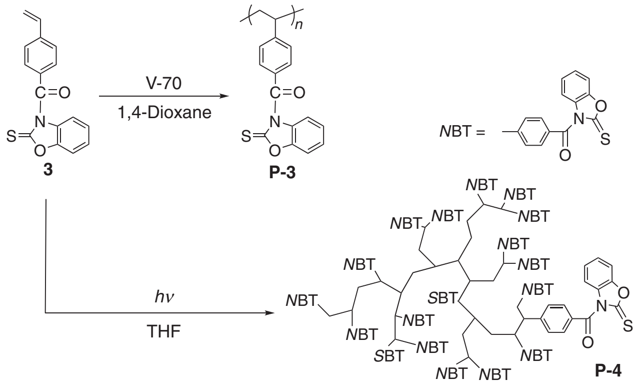
Scheme 1. Thermal rearrangement of **2** to **5**.

The thermal rearrangement reaction from *S*-(2-benzoxazolyl) thioester to 3-acylbenzoxazoline-2-thione was confirmed using model compound **2** (Scheme 1). **2** exhibited a sharp exothermic at 101 °C and an endotherm at 112 °C, which reflect melting point and thermal rearrangement of **2**, respectively. The melting point and spectroscopic data of compound obtained from thermal rearrangement of **2** was identical with the authentic *N*-acyl derivative **5**.

The styrene monomer, *S*-(2-benzoxazolyl)-4-vinylthiobenzoate (**1**), was synthesized by the reaction of 4-vinylbenzoyl chloride and 2-sulfanylbenzoxazole with triethylamine (TEA) in THF at below 10 °C. The polymerization of **1** was carried out as a free radical polymerization with 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) as the initiator in 1,4-dioxane at 30 °C for 18 h, to afford a homopolymer **P-1** with $M_\mathrm{n} = 1.7 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 2.29$, in 58% yield (Scheme 2). **1** has an interesting structure because it contains a polymerizable styrene group and an initiating/propagating moiety consisting of a benzoxazolylthio (BT) group. Photolysis of **1** leads to the initiating benzoyl radical with inactive BT radical. This benzoyl radical can react with the vinyl group to form dimer-like structure (ABB′ monomer).[14] Branched polymer (**P-2**, $M_\mathrm{n} = 5.2 \times 10^3$, $M_\mathrm{w}/M_\mathrm{n} = 2.83$) with terminal *S*-benzoxazolyl thiobenzoate (*S*BT) was synthesized by photoinitiated radical polymerization of **1** with *S*-(2-benzoxazolyl)-4-methoxythiobenzoate as a capping agent[15] (**2**, 2 mol %) at room temperature in 26% yield (Scheme 2). The structures were confirmed by



Scheme 2. Selective synthesis from **1** of linear and branched polymers bearing *S*-(2-benzoxazolyl) thioester moieties.

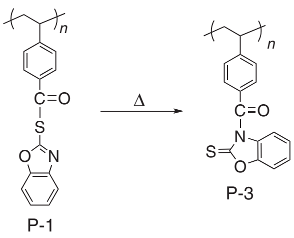


Scheme 3. Selective synthesis from **3** of linear and branched polymers bearing 3-acylbenzoxazoline-2-thione moieties.

^{1}H NMR and FT-IR spectroscopy.[16] The FT-IR spectrum showed a characteristic absorption peak at 1702 cm^{-1} due to the carbonyl groups.

In order to confirm the structures of the products obtained by thermal reaction of the above polymers, we also synthesized authentic samples of the *N*-acyl-type polymers from 3-(4-vinylbenzoyl)benzoxazoline-2-thione (**3**) as a monomer, using the same methods. Linear polymer **P-3** ($M_n = 2.3 \times 10^4$) and branched polymer **P-4** ($M_n = 1.7 \times 10^4$) were obtained in 79 and 20% yield, respectively (Scheme 3). The FT-IR spectra showed a clear shift of the carbonyl vibration ($\nu_{C=O}$) toward higher wavenumber (around 1717 cm^{-1}) for **P-3** and **P-4** compared to **P-1** and **P-2**.

The thermal rearrangement of the *S*-acyl moieties in thin films of **P-1** and **P-2** (Scheme 4) was followed by means of FT-IR spectroscopy. Figures 1a and 1b show the FT-IR spectra of **P-1** before and after heating at 135 °C for 30 min.[17] The non-heated film shows characteristic signals of the carbonyl groups of the *S*-acyl groups at 1702 cm^{-1} (Figure 1a). After heating, the carbonyl vibrational band shifted to 1717 cm^{-1}. In addition, the vibrational band at 1353 cm^{-1} assigned to thiocarbonyl ($\nu_{C=S}$) groups became more intense. Similar results were obtained with **P-2**. FT-IR spectra of **P-1** and **P-2** after heating coincided well with those of **P-3** and **P-4**, synthesized separately as authentic standards. Further, as shown in Figure 2, heating of a film of **P-1** caused a significant increase in the absorption at around 340 nm, which can be attributed to the formation of 3-acylbenzoxazoline-2-thione groups.[18,19] It is noteworthy that the previously used photo-Fries rearrangement[3–5] is accompanied with photodecarboxylation, whereas the present thermal rearrangement proceeded selectively without any side reaction.



Scheme 4. Thermal rearrangement of **P-1** to **P-3**.

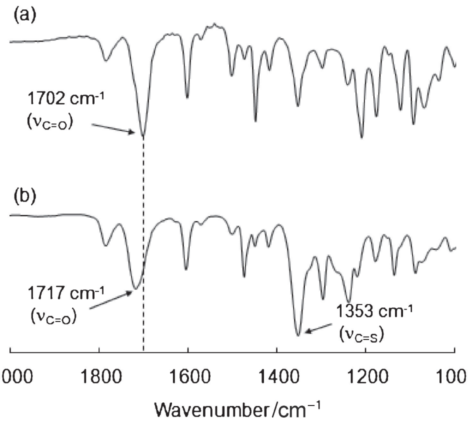


Figure 1. FT-IR spectra of **P-1**; (a) prior to heating, and (b) after heating at 135 °C for 30 min.

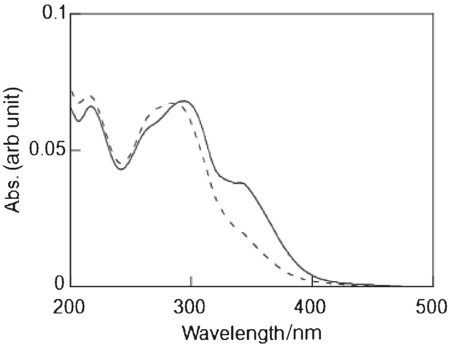


Figure 2. UV–vis spectra of a film of **P-1** on a quartz cell. Broken line: prior to heating (**P-1**); solid line: after heating at 135 °C for 10 min.

A chloroform solution of the polymer was spin-coated onto a silicon wafer and dried in vacuo at room temperature to prepare a thin film with a thickness of about 0.1 µm. The refractive indices of polymer films were investigated by means of ellipsometry before and after heating at 135 °C for 10 min. The values of n_b (refractive index before heating), n_a (refractive index after heating), and Δn (the change of refractive index) are summarized in Table 1.

After thermal rearrangement of **P-1**, the refractive index at $\lambda = 632.8$ nm changed from $n_b = 1.675$ to $n_a = 1.687$ ($\Delta n =$

Table 1. Refractive index properties of thin films of polymers[a]

Polymers	n_b[b]	n_a[c]	Δn[d]
P-1	1.675	1.687	+0.012
P-2	1.674	1.684	+0.010

[a]The thin films (about 0.1 µm in thickness) were prepared from the $CHCl_3$ solution, followed by spin-coating onto a silicon wafer. [b]Refractive index before heating. [c]Refractive index after heating at 135 °C for 10 min. [d]$\Delta n = n_a - n_b$.

+0.012). In the case of **P-2**, Δn was +0.010 after heating. Notably, n values obtained after heating were almost identical with those of authentic **P-3** ($n = 1.684$) and **P-4** ($n = 1.683$), suggesting that the rearrangement from the *S*-acyl to *N*-acyl groups proceeds efficiently upon heating. The n_b value of the branched polymer was lower than that of the linear polymer, possibly because the three-dimensional globular structure of the branched polymer results in a lower density (ρ), leading to a lower value of n according to the Lorentz–Lorenz equation (see above). We also measured the refractive index change of monofunctional compound **2** and difunctional *S*,*S*′-(2-benzoxazolyl) dithioisophthalate (**4**, see Supportin Information[22]) dispersed in a poly(methyl methacrylate) (PMMA) matrix. Films prepared with a ratio of **2**/PMMA and **4**/PMMA of 2 (wt/wt) showed Δn values of +0.015 and +0.017 after heating, with retention of good film quality.[20] Film prepared with a **4**/PMMA ratio of 1 (wt/wt) showed Δn of +0.005. These results support the idea that thermal rearrangement of *S*-thioester groups is associated with refractive index changes. The change of refractive index for model compounds **2** and **5** (Scheme 1) is also consistent with computational prediction.[21]

In summary, linear and branched polymers bearing active *S*-thioester moieties were selectively synthesized by means of free radical and photoinitiated radical polymerization, respectively, starting with *S*-(2-benzoxazolyl)-4-vinylthiobenzoate. The refractive index n of thin films of both these polymers increased ($\Delta n \approx +0.01$) upon heating, as a result of thermal rearrangement of the *S*-(2-benzoxazolyl) thioester moieties to 3-acylbenzoxazoline-2-thione moieties. Thermal rearrangement reaction of functional groups in polymers is a new strategy for creating materials whose refractive index can be changed. It should be possible to stimulate such reaction by applying a laser beam as the heat source. The products, i.e., polymers having *N*-acyl moieties, can react with amine derivatives, and this might result in further modification of Δn. Other polymers containing *S*-acyl derivatives are currently under investigation.

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21 Computationally predicted n values for **2** and **5** by using ACD/ChemSketch are 1.674 and 1.702, respectively.
22 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.