Photoinduced Stereomutation

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Photoinduced Racemization of an Optically Active Helical Polymer Formed by the Asymmetric Polymerization of 2,7-Bis(4-*tert*-butylphenyl)fluoren-9-yl Acrylate**

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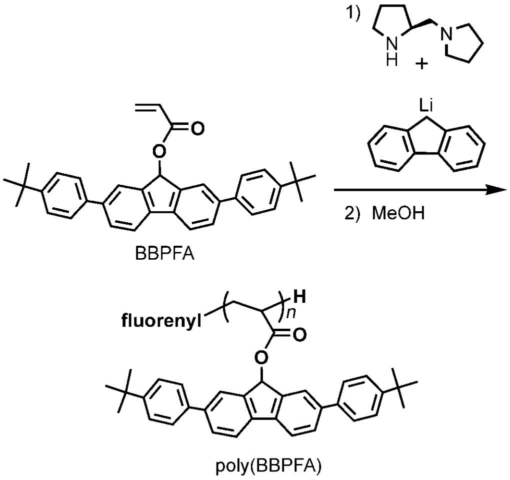
The helix is a fundamental macromolecular structure. The construction and mutation of helical structures have been studied for a variety of synthetic polymer systems.[1] Macromolecular stereomutation is triggered by chemical or thermal stimuli in most cases, and fewer examples are known of stereomutation triggered by light. Existing examples of photoinduced stereomutation involve photochromic groups incorporated into the side chains or main chain of polymers. These groups cause the isomerization of a double bond[2–4] or bond cleavage and formation.[5]

Herein we report the synthesis of optically active preferred-handed helical poly(2,7-bis(4-*tert*-butylphenyl)fluoren-9-yl acrylate) (poly(BBPFA)), a novel polyacrylate, and its effective racemization induced by photoirradiation. In contrast to the previous examples,[2–5] the stereomutation observed for this polymer is governed by simple rotation about the single bonds between the side-chain fluorenyl moieties and the *tert*-butylphenyl substituents without any changes in chemical bonding.

Polymerization was carried out with the complex formed between 9-fluorenyllithium (FlLi) and (+)-1-(2-pyrrolidinylmethyl)pyrrolidine (PMP) as the initiator in toluene at −78 °C (Scheme 1, Table 1). This initiator system has been used to synthesize preferred-handed helical polymers from bulky (meth)acrylates.[1a,b,6] The polymerization of BBPFA occurred with almost quantitative monomer conversion. The observed increase in M_n with an increase in the [BBPFA]/[FlLi] ratio (from 10:1 to 40:1) implies that the polymerization has "living" characteristics to a certain extent. Polymerization was also attempted at a [BBPFA]/[FlLi] ratio of 60; however, the reaction system gelled owing to poor solubility of the products, and relatively low monomer conversion (37%) resulted.



Scheme 1. Asymmetric polymerization of BBPFA.

Table 1: Asymmetric anionic polymerization of BBPFA with FlLi–PMP in toluene at −78 °C.[a]

Entry	[BBPFA]/[FlLi]	Conv.[b] [%]	Yield[c] [%]	M_n[d]	M_w/M_n[d]	$[\alpha]_{435}$[e] [°]	$[\alpha]_D$[e] [°]
1	10	>99	93	2830	1.09	+6	+2
2	20	>99	92	8010	1.23	+162	+28
3	40	>99	90	12730	1.48	+213	+35

[a] Reaction conditions: $[\text{monomer}]_0 = 0.108\ \text{mol L}^{-1}$, [PMP]/[FlLi] = 1.2, 24 h (entries 1 and 2) or 48 h (entry 3). [b] Conversion was determined by ^{1}H NMR spectroscopic analysis of the reaction mixture. [c] Yield of the methanol-insoluble portion of the product mixture. [d] The number-average molecular weight and the polydispersity index were determined by SEC in THF with polystyrene as the standard. [e] The values of optical rotation were determined in $CHCl_3$ at room temperature (concentration: 0.50 g dL^{-1}, cell length: 1 dm).

The obtained polymers were optically active and exhibited intense circular dichroism (CD) spectra (Figure 1). Optical activity and CD intensity increased with an increase in the M_n value of the polymer. These results, combined with the fact that BBPFA monomer does not have any configurational chirality, strongly suggest that the observed chiroptical properties can be ascribed to a preferred-handed helical polymer conformation. This conclusion is supported by the

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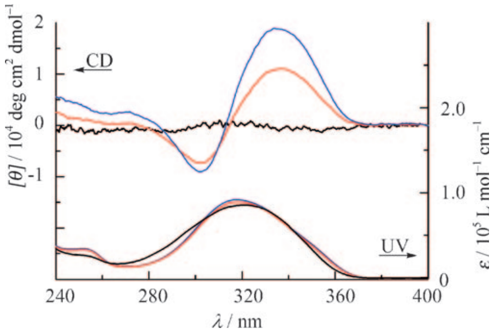

Figure 1. CD and UV spectra of poly(BBPFA) with different M_n values in tetrahydrofuran: blue $M_n = 12730$, red $M_n = 8010$, black $M_n = 2830$.

very broad signals observed in the ^{1}H NMR spectrum of the polymer; the broadness of the signals indicates a rigid conformation of the polymer chain (see the Supporting Information). Only acrylate monomers with bulky tertiary ester groups[6c,d] have previously been reported to afford preferred-handed helical polyacrylates. Hence, poly(BBPFA) may be the first polyacrylate with a secondary side-chain group to have a helical conformation. The helix-sense excess of poly(BBPFA) is not yet known: it may potentially be determined by the method used for the chromatographic resolution of poly(triphenylmethyl methacrylate).[6e]

Although BBPFA monomer does not have configurational chirality, axial chirality may result from a twisted conformation of the two biphenyl moieties in the 2,7-bis(4-*tert*-butylphenyl)fluorenyl group. X-ray crystal-structure analysis of the monomer revealed that the biphenyl moieties are twisted, with a dihedral angle of 27°[7] (Figure 2). Although the monomer has a *meso* twist conformation in the crystal, a chiral, preferred-handed twist conformation may be adopted during the process of asymmetric polymerization. This behavior is suggested by the split-type CD pattern in the longer-wavelength range. This type of pattern is often observed for chromophores with a chiral, twisted spatial arrangement. Hence, we propose that optically active poly(BBPFA) not only has a preferred-handed helical main-chain conformation, but also that the side-chain biphenyl moieties have a preferred-handed twist conformation.

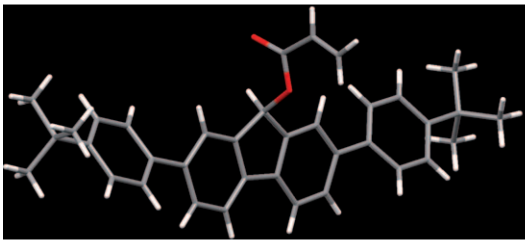

Figure 2. Crystal structure of BBPFA monomer.

During the course of analytical studies of the chiroptical properties of the polymers, the CD intensity of solutions of poly(BBPFA) in THF was found to decrease gradually on standing at room temperature in ambient light. Since no clear decomposition of the polymers was detected, we concluded that this mutarotation was due to conformational transition (stereomutation) of the polymer chain.

To identify the cause of the stereomutation, we examined heat and light as possible stimuli. When we heated a solution in THF of the polymer from entry 2 in Table 1 (at a concentration of 1.16×10^{-4} mol L^{-1} with respect to the monomeric residues) at 60 °C for 6 h in the dark, no change was evident in the CD spectrum. In contrast, the peaks in the CD spectrum of the same polymer in THF (2.26×10^{-4} mol L^{-1} with respect to the monomeric residues) nearly completely disappeared within 4 min when the solution was irradiated with a 500 W Xe–Hg lamp monochromatized at 320 nm (Figure 3). These results clearly indicated that light had induced the stereomutation. Interestingly, however, irradiation at 254 nm for 12 h had no effect on the CD spectrum of the polymer.

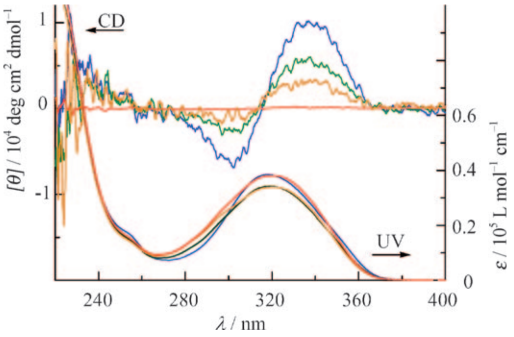

Figure 3. CD and UV spectra of poly(BBPFA) ($M_n = 8010$) in tetrahydrofuran after photoirradiation at 320 nm for 0 (blue), 2 (green), 3 (orange), and 4 min (red). (Concentration: 2.26×10^{-4} mol L^{-1} with respect to the monomeric residues; cell length: 1 mm).

Upon irradiation at 320 nm, the UV spectrum of the polymer showed little change; thus, it appeared that the chemical structure of the polymer was not affected. This conclusion was supported by analysis of the polymer by size-exclusion chromatography (SEC) before and after photoirradiation: virtually no change in peak shape and position was observed after irradiation (see the Supporting Information).

The mutarotation tended to be faster at a lower concentration; thus, chain aggregation appears to retard the mutation. In fact, no clear CD absorptions were observed for the polymer from entry 2 in Table 1 in THF at a concentration of 2.26×10^{-5} mol L^{-1} (with respect to the monomeric residues) even immediately after dissolution (see the Supporting Information). Ambient light probably caused rapid stereomutation in this case.

We assume that the stereomutation is triggered by photoexcitation of the side-chain chromophores of poly(BBPFA), which leads to a conformational transition of the two biphenyl moieties in the side-chain groups from a twisted form to the coplanar form. A twist–coplanar transition upon photoexcitation has been reported for the biphenyl compound.[8] This type of transition would lead to racemization of the proposed preferred-handed twist of the side-chain biphenyl moieties of poly(BBPFA). This assumption is supported by the fact that mutarotation was effected by irradiation not at 254 nm but at 320 nm, that is, within the longer-wavelength band of the UV spectrum. HOMO–LUMO interactions should contribute to transitions in this region of the UV spectrum. As HOMO and LUMO orbitals are delocalized over the biphenyl moieties (see the Supporting Information), it is very likely that light with a wavelength of 320 nm induces the conformational transition of the biphenyl moieties.

Upon the twist–coplanar transition of the side-chain biphenyl moieties, this information would be transferred to the helical backbone of the polymer chain to cause total racemization of the preferred-handed helix into an equimolar mixture of right- and left-handed helices. This hypothesis was supported by the resolution of a polymer that had been subjected to photoirradiation and showed no CD absorptions into dextrorotary and levorotatory fractions by HPLC on a chiral stationary phase. The known preferred-handed helical polymer poly(1-(*p*-vinylphenyl)dibenzosuberyl methacrylate)[9] was subjected to HPLC under the same conditions for comparison (Figure 4). If the stereomutation took place only in the side chain, and the main-chain helix remained preferred-handed, HPLC resolution of the stereomutation products would not be possible. Furthermore, an optically inactive poly(BBPFA) ($M_n = 6000$, $M_w/M_n = 2.50$) prepared as an authentic racemic mixture by radical polymerization with α,α′-azobisisobutyronitrile in chloroform at 60 °C was also resolved by using the same HPLC setup.

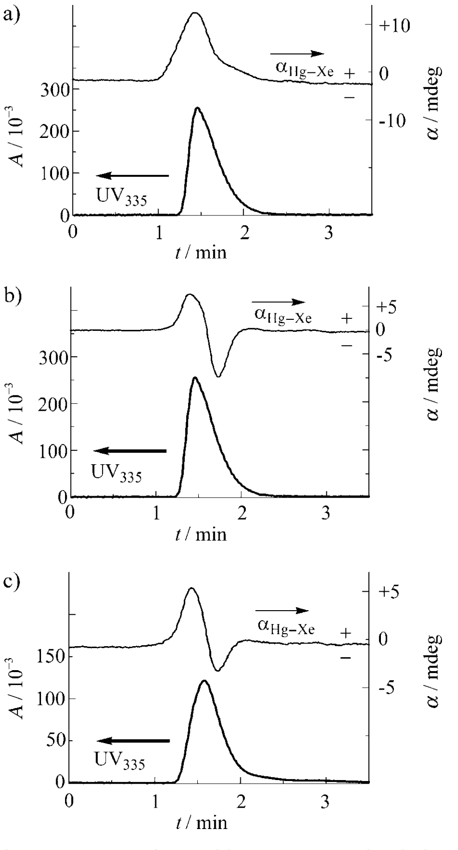

Figure 4. Chromatograms obtained by HPLC on a chiral phase for a) the polymer from run 2 in Table 1 before photoirradiation, b) the same polymer after photoirradiation at 320 nm for 4 min, and c) an authentic sample of the racemic polymer prepared by free-radical polymerization ($M_n = 6000$, $M_w/M_n = 2.50$). In each case, the top and bottom chromatograms were obtained with polarimetric (α_{Hg-Xe}) and UV detectors (335 nm, absorbance in absorbance units), respectively. (Column size: 15 cm × 0.21 cm (inner diameter); eluent: chloroform; temperature: 0 °C; flow rate: 0.5 mL min^{-1}.)

Molecular-mechanics simulations on poly(BBPFA) 20-mer models indicated that combinations of a right- or left-handed main chain with a randomly twisted (racemized) side chain had similar steric energies and were more stable than other combinations involving the preferred-handed or *meso* twisted side chain (see the Supporting Information). Therefore, the proposed mechanism, according to which side-chain racemization leads to main-chain racemization, is energetically rational.

Although the racemization of optically active 1,1′-biphenanthrenes by photoirradiation[10] and the racemization of preferred-handed helical polymers by thermal and chemical stimuli[11] have been reported previously, this study, to the best of our knowledge, provides the first example of the photoinduced racemization of a preferred-handed helical polymer without any rearrangement of chemical bonds, such as bond formation, bond cleavage, or the isomerization of a double bond. Studies are in progress towards the elucidation of the complete mechanism of the stereomutation, the development of a reversible stereomutation with circularly polarized light, and the application of poly(BBPFA) for the construction of photoswitching materials.

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[7] Data were collected on a Rigaku R-AXIS RAPID imaging plate with $\mathrm{Cu}_{K\alpha}$ radiation ($\lambda = 1.54180$ Å). Crystallographic data for BBPFA: $C_{36}H_{37}O_{2.5}$, $M = 509.69$, triclinic, $P\bar{1}$(#2), $a = 13.3259$(2), $b = 14.7783(3)$, $c = 16.4711(7)$ Å, $\alpha = 87.6796(7)$, $\beta = 83.4839(7)$, $\gamma = 63.8822(7)$, $V = 2893.52(14)$ Å^3, $\mu = 0.557$ mm^{-1}, $T = 93.1$ K, 38963 collected reflections, 10293 unique reflections, $R_{\mathrm{int}} = 0.023$, $R1 = 0.0711$ (for 8170 reflections with $I > 2\sigma(I)$), $wR2 = 0.2130$ (all data). CCDC 742495 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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