Synthesis of New Photoresponsive Polymers Containing Trifluoromethyl-Substituted Norbornadiene Moieties

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Polymers containing trifluoromethyl (CF_3)-substituted donor–acceptor NBD moieties in the side chain or in the main chain were synthesized by substitution or addition with CF_3-NBD-carboxylic acid derivatives, or by polycondensation of CF_3-NBD-dicarboxylic acid derivatives, and the durability of the resulting polymers was examined.

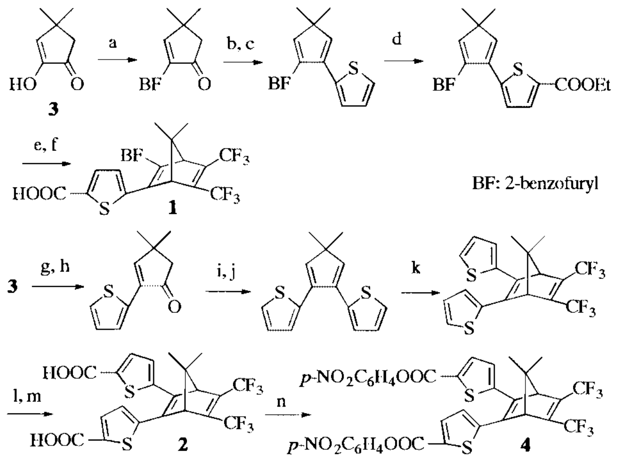
Photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) is of interest as a solar energy conversion and storage system,[1] because photoenergy can be stored as strain energy (about 20 kcal/mol) in a QC molecule (Scheme 1). Recently, this photochemical reaction has also been investigated as an optical waveguide utilizing photoinduced refractive index changes[2a,b] or as a photochromic system potentially applicable to data storage.[2c]

Taking these unique characteristics of NBD into account, polymers containing NBD moieties have been investigated. However, the photoreactivity and the fatigue resistance of these polymers were insufficient for practical use as advanced materials.[3] Recently, we reported the synthesis of CF_3-substituted donor–acceptor NBD (CF_3-NBD) derivatives which not only absorb visible light efficiently but also exhibit efficient fatigue resistance.[4] Therefore, we now synthesized new photoreactive polymers containing CF_3-NBD moieties.

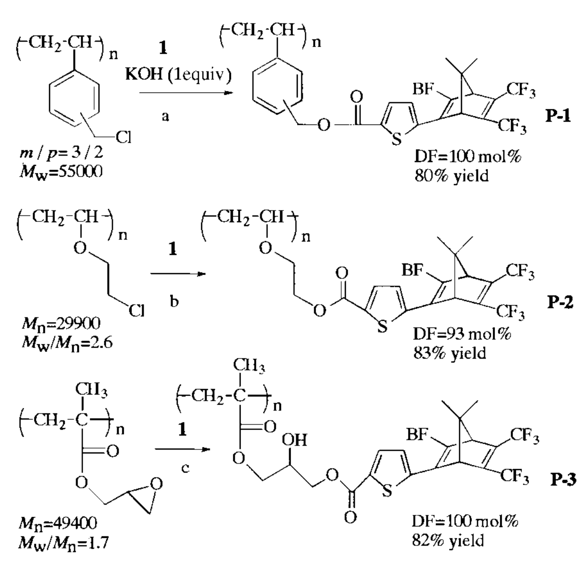
The NBD monomers, namely, NBD carboxylic acid **1** and NBD dicarboxylic acid **2**, were synthesized from cyclopentanedione derivative **3** as shown in Scheme 1.[5]

Polymers containing CF_3-NBD moieties in the side chain were synthesized according to Scheme 2.[5] The reactions of NBD carboxylic acid **1** with poly(chloromethylstyrene),[3b] poly(2-chloroethyl vinyl ether) [3c], and poly(glycidyl methacrylate) [3d] proceeded smoothly using tetrabutylammonium bromide as a catalyst in DMF to give the corresponding polymers **P-1**, **P-2**, and **P-3** in 80, 83, and 82% yields, respectively. To **P-1**, **P-2**, and **P-3**, NBD carboxylic acid was found to be introduced in 100, 93, and 100% yield, respectively. [6] These results show that CF_3-NBD moieties could be readily introduced in the side chain of many polymers.

Next, we synthesized polymers containing CF_3-NBD moieties in the main chain as shown in Tables 1 and 2. [5] Polyamide **P-4** was synthesized by polycondensation of the bis(4-nitrophenyl) ester **4**, obtained from NBD dicarboxlic acid **2**, with *trans*-1,4-diaminocyclohexane as diamine.[7] The yield and the M_n of **P-4** were 82% and 17800, respectively. [8] This polyamide was also synthesized from **2** with diamine using DPPA as condensation reagent; the yield and the M_n were 88% and 42,900, respectively. Polyester was synthesized by polycondensation of **2** with diol using hafnium chloride as the Lewis acid catalyst.[9] The yield and the M_n of **P-5** were 82% and 39,300, respectively. On the other hand, when the reaction was carried out using WSCD



Scheme 1. Reagents and conditions : a) Ref. 4; b) 2-lithiothiophene, THF, –78 ℃, 91%; c) *p*-TsOH, toluene, reflux, 78%; d) *n*-BuLi, ClCOOEt, THF, –78 ℃, 83%; e) Hexafluoro-2-butyne, toluene, room temp, 96%; f) 1M NaOH, THF, 50 ℃, 96%; g) 2-lithiothiophene, THF, –78℃, 82%; h) *p*-TsOH, toluene, reflux, 90%; i) 2-lithiothiophene, THF, –78 ℃, 87%; j) *p*-TsOH, toluene, reflux, 79%; k) Hexafluoro-2-butyne, toluene, 50 ℃, 99%; l) *n*-BuLi, ClCOOEt, THF, –78 ℃, 49%; m) 1M NaOH, THF, 50 ℃, 80%; n) *p*-nitrophenol, WSCD, DMAP, CH_2Cl_2, room temp, 60%.



Scheme 2. Reagents and conditions: a)TBAB (0.1 equiv), DMF, 80 ℃, 48 h, 80%, DF (degree of functionality) = 100%; b) K_2CO_3 (3equiv), TBAB (1equiv), DMF, 90 ℃, 72 h, 83%, DF =93%; c) TBAB (0.1 equiv), DMF–*i*-PrOH (20:1), 80 ℃, 48 h, 82%, DF =100%.

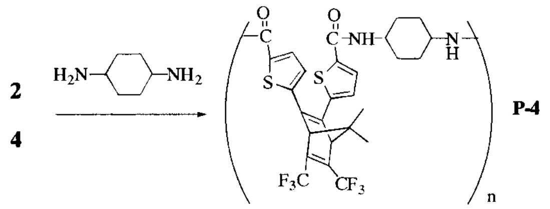


Table 1. Synthesis of polyamide containing CF_3-NBD moieties

Reagent and conditions	Yield/%	$M_n^b\times10^{-4}$	M_w/M_n^b
4, DMF, rt, 4d	82	1.78	1.96
2, DPPA[a], Et_3N, DMF, rt, 2d	88	4.29	5.77

[a]Diphenylphosphoryl azide. [b]Estimated by GPC based on polystyrene standards (eluent: DMF).

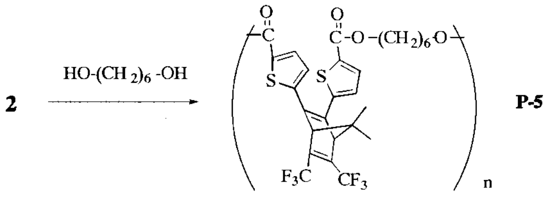


Table 2. Synthesis of polyester containing CF_3-NBD moieties

Reagent and conditions	Yield/%	$M_n^c\times10^{-4}$	M_w/M_n^c
2, $HfCl_4 \cdot THF_2$ (0.2equiv), *o*-xylene, reflux, 2d	82	3.93	2.33
2, WSCD[a], DMAP[b], CH_2Cl_2, rt, 2d	88	1.83	2.32

[a]Dimethylaminopropylethylcarbodiimide hydrochloride. [b]Dimethylaminopyridine. [c]Estimated by GPC based on polystyrene standards (eluent: DMF).

as condensation reagent, the M_n of **P-5** was 18,300.

As shown in Figure 1 and Table 3, these polymers had a large absorption band in the visible region.

We also examined the durability of the CF_3-NBD moieties in the polymer for repeated cycles of interconversion. Recently, we reported that CF_3-NBD derivatives had efficient fatigue resistance.[4] As shown in Figure 2, the CF_3-NBD moieties in **P-3** possessed good fatigue resistance and the degradation of the NBD moieties was 55% after 1000 cycles.[10]

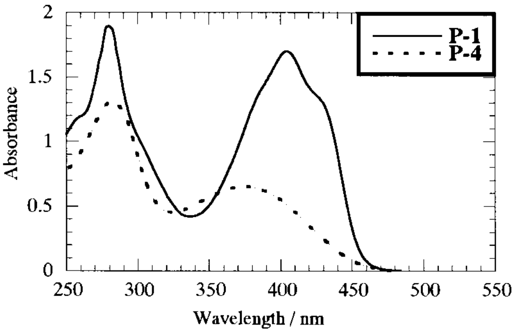


Figure 1. Absorption spectra of **P-1** and **P-4**. (1×10^{-4} mol dm^{-3} solution in THF.)

Table 3. Absorption spectral data of polymers containing CF_3-NBD moieties

No. of polymers	λ_{max}/nm (log ε)[a]	λ_{edge}/nm [a,b]
P-1	405 (4.2)	505
P-2	405 (4.2)	505
P-3	404 (4.2)	505
P-4	379 (3.8)	503
P-5	385 (3.8)	505

[a]1×10^{-4} mol dm^{-3} solution in THF. [b]ε = 10

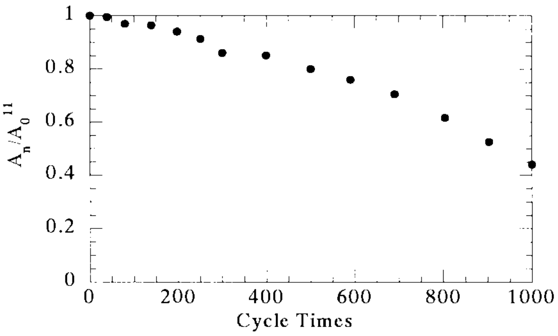


Figure 2. Durability of **P-3**.[11]

In conclusion, polymers containing CF_3-NBD moieties in the side chain or in the main chain were synthesized by substitution or addition of CF_3-NBD carboxylic acid derivatives, or by polycondensation of CF_3-NBD dicarboxylic acid derivatives, respectively. These polymers had a large absorption band in the visible region. The CF_3-NBD moieties in these polymers showed resistivity to repeated cycles of interconversion.

References and Notes

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5 The structure of the new compounds was confirmed by MS, IR, and NMR spectra.
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8 M_n and M_n/M_w were estimated by GPC based on Polystyrene standard.
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10 Preparation of polymer film: A solution of polymer (7.4 mg) in chloroform (1 mL) was degassed by three consecutive freeze-pump-thaw cycles and cast on a quartz plate. Then, the quartz plate-cast polymer was dried in vacuo at 80 °C for 15 h. Furthermore, a solution of PMMA chloroform was cast on the film and dried in the same way as above. Examination of the durability: The experiment was performed under argon atmosphere. Initially, the polymer film was irradiated by a 500-W xenon lamp (Ushio Electric Co., UI-502Q) until the disappearance of the absorbance of the absorption maxima. Then, the film containing the corresponding QC moieties was heated on a hot plate until the reversion of the absorbance of the NBD moieties (irradiated for 2 min, then heated at 80 °C for 20 min).
11 A_0 and A_n are the differences in the absorbance values between NBD moieties and QC moieties in the polymer at λ_{max} of the NBD moieties on the 1st and nth cycles of reactions, respectively.