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Synthesis of New Photoresponsive Polymers Containing Trifluoromethyl-Substituted Norbornadiene Moieties

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Polymers containing trifluoromethyl (CF₃)-substituted donor-acceptor NBD moieties in the side chain or in the main chain were synthesized by substitution or addition with CF₃-NBD-carboxylic acid derivatives, or by polycondensation of CF₃-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, 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 or as a photochromic system potentially applicable to data storage.

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. Recently, we reported the synthesis of CF₃-substituted donor-acceptor NBD (CF₃-NBD) derivatives which not only absorb visible light efficiently but also exhibit efficient fatigue resistance. Therefore, we now synthesized new photoreactive polymers containing CF₃-NBD moieties.

The NBD monomers, namely, NBD carboxylic acid 1 and NBD dicarboxylic acid 2, were synthesized from cyclopentanone derivative 3 as shown in Scheme 1. The reactions of NBD carboxylic acid 1 with poly(chloromethylstyrene), poly(2-chloroethyl vinyl ether) and poly(glycidyl methacrylate) proceeded smoothly using tetrabutylammonium bromide as a catalyst in DMF to give the corresponding polymers P·I, 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. These results show that CF₃-NBD moieties could be readily introduced in the side chain of many polymers.

Next, we synthesized polymers containing CF₃-NBD moieties in the main chain as shown in Tables 1 and 2. Polyamide P·4 was synthesized by polycondensation of the bis(4-nitrophenyl) ester 4, obtained from NBD dicarboxylic acid 2, with trans-1,4-diaminocyclohexane as diamine. The yield and the Mₙ of P·4 were 82% and 17,800, respectively. This polyamide was also synthesized from 2 with diamine using DPPA as condensation reagent; the yield and the Mₙ were 88% and 42,900, respectively. Polyester was synthesized by polycondensation of 2 with diol using hafnium chloride as the Lewis acid catalyst. The yield and the Mₙ 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 °C, 91%; c) p-TsOH, toluene, reflux, 78%; d) n-BuLi, CICOEt, THF, -78 °C, 83%; e) Hexafluoro-2-butyne, toluene, room temp, 96%; f) 1M NaOH, THF, 50 °C, 96%; g) 2-lithiothiophene, THF, -78 °C, 82%; h) p-TsOH, toluene, reflux, 90%; i) 2-lithiothiophene, THF, -78 °C, 87%; j) p-TsOH, toluene, reflux, 79%; k) Hexafluoro-2-butyne, toluene, 50 °C, 99%; l) n-BuLi, CICOEt, THF, -78 °C, 49%; m) 1M NaOH, THF, 50 °C, 80%; n) p-nitrophenol, WSCD, DMAP, CH₂Cl₂, room temp, 60%.

Scheme 2. Reagents and conditions: a) TBAB (0.1 equiv), DMF, 80 °C, 48 h, 80%, DF (degree of functionality) = 100% b) K₂CO₃ (Eqquiv), TBAB (1 equiv), DMF, 90 °C, 72 h, 83%, DF =93%; c) TBAB (0.1 equiv), DMF = i-ProOH (20:1), 80 °C, 48 h, 82%, DF =100%.

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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
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., U1-502Q) until the disappearance of the absorbance of the QC moieties. 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$_1$ and A$_n$ are the differences in the absorbance values between NBD moieties and QC moieties in the polymer at $\lambda_{\text{abs}}$ of the NBD moieties on the 1st and nth cycles of reactions, respectively.