SYNTHESIS OF SOLAR ENERGY STORAGE-EXCHANGE POLYMERS AND THEIR PHOTOCHEMICAL PROPERTIES

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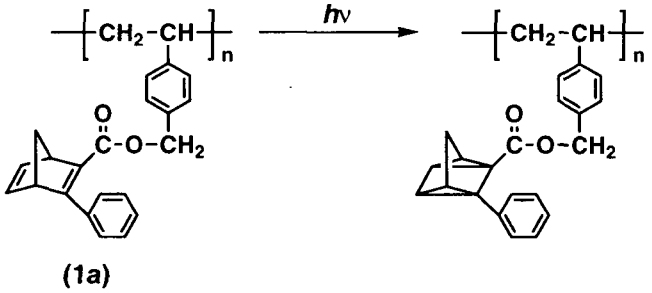
Petroleum, natural gas and coal are currently very useful fossil resources to keep our comfortable and healthy life styles; however, there are of course limitations in the long run. Recently, it has also been pointed out that combustion of such fuels causes serious environmental problems such as warming of the earth due to the produced carbon dioxide and acid rain due to incomplete combustion. Thus, it is very important to reduce the use of these fossil resources, especially as fuels, and furthermore to keep them as long term resources for non-fuel purposes. Therefore, development of new energy resources has become a very important subject for us, and sunlight has been promoted as essentially a clean and limitless supply of energy.

Although there are many proposals as to have to tap solar energy, photochemical valence isomerization between norbornadiene (NBD) derivatives and the corresponding quadricyclane (QC) derivatives has become of increasing interest[1] as one of the chemical reaction systems for solar energy conversion and storage. This is because, as shown in the above systems, NBD molecule can store solar energy as strain energy in a QC molecule and then the QC molecule can release about 96 kJ/mol of thermal energy upon contact with certain catalysts, upon irradiation with UV light, or by heating. It has been further proposed[2] that polymers containing NBD moieties could be used in new photo-switch and other photo-devices due to their refractive index changes upon photo-irradiation, which was recently confirmed[3] experimentally

Since 1986, from this background, my research group has investigated[4] the synthesis and photochemical reaction of polymers containing NBD moieties in the main chain or the side chain. Polymers (1) containing pendant NBD moieties in the side chain were synthesized[2,4-6] by the substitution reaction of poly[(*p*-chloromethyl)styrene] with certain NBD derivatives such as 3-potassium phenyl-2,5-NBD-2-carboxylate using phase transfer catalysis. A similar polymer (2) containing pendant NBD moiety was synthesized[7] by the selective cationic polymerization of 2-[[(3-phenyl-2,5-norbornadienyl)-2-carbonyl]oxy]ethyl vinyl ether. Polyesters (3) containing pendant NBD moieties were also synthesized[8,9] by the alternating ring-opening copolymerization of glycidyl ester containing NBD moieties with carboxylic anhydrides using quaternary onium salts as catalysts. Most of the synthesized polymers containing pendant NBD moieties showed high photochemical reactivity, and the pendant NBD moieties on the polymers were converted quantitatively to the corresponding QC groups upon photo-irradiation for 3-10 minutes (Scheme 1).



(1a)

Scheme 1

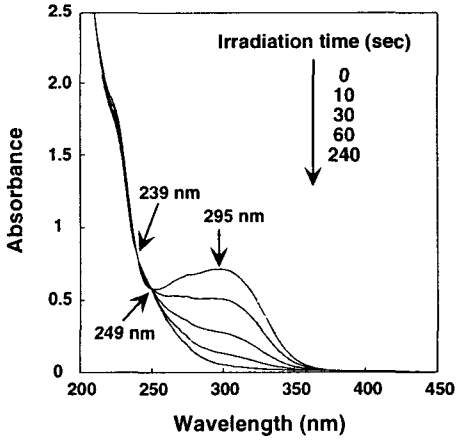


Figure 1. Change of UV spectra of **1a** in the film state upon irradiation with a xenon lamp (2.00~2.10 mW/cm^2 at 310 nm).

Polyamides (5) containing NBD moieties in the main chain were synthesized by polycondensations of 2,5-NBD-2,3-dicarboxylic acid (NBDC) with diamines[10] or