JOC Notes

Synthesis and Characterization of a New Benzofulvene Polymer Showing a Thermoreversible Polymerization Behavior

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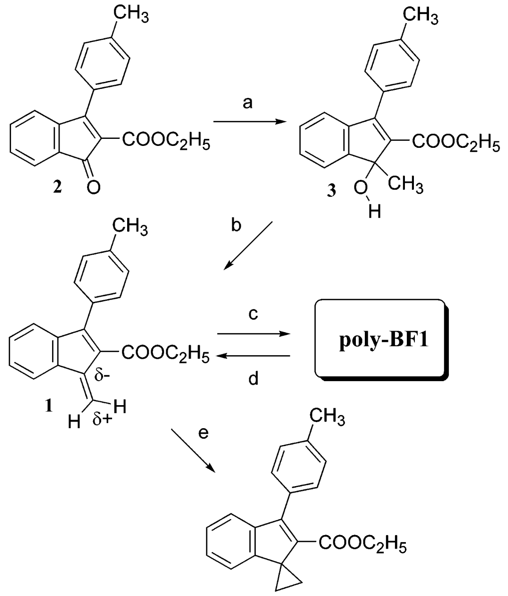
Abstract: A new polymer based on a functionalized benzofulvene moiety has been synthesized by spontaneous polymerization of the monomer in the solid state. This polymer shows a very high molar mass, high solubility in the most common organic solvents, and thermoreversible polymerization properties. An interesting application in synthesis is reported.

In the chemistry of advanced polymers, the properties of polydibenzofulvenes, polythiophenes, polypyrroles, polyfulvenes, and self-organized assemblies of polythiophenes are of current interest.[1−3]

Recently, benzofulvene derivative **1** (**BF1**) has been discovered to form a new macromolecular architecture that is potentially useful in the chemistry of advanced polymers. In this paper, we describe the synthesis, the preliminary characterization, and useful synthetic application of the new polymer based on the benzofulvene moiety.

SCHEME 1[a]



[a] Reagents: (a) CH_3MgBr, $C_2H_5OC_2H_5$; (b) PTSA, $CHCl_3$; (c) solvent elimination; (d) solvent, heating; (e) CH_2N_2, $(CH_3COO)_2Pd$, $CHCl_3$.

In a large research program devoted to the discovery of new drugs, we were interested in the synthesis of **1**. This *trans*-diene represented a very interesting intermediate for the preparation of a variety of useful building blocks to be used in the synthesis of new potentially bioactive compounds. Thus, we engaged the synthesis of **1** following the procedure outlined in Scheme 1. The key indenone intermediate **2**[4] was prepared by modifying the procedure described by Koelsch,[5] and its structure was unambiguously characterized by means of single-crystal X-ray diffractometry studies (Supporting Information). The reaction of **2** with methylmagnesium bromide gave the expected indenol **3** (the structure of this 1,2-addition product was solved by X-ray diffraction). Dehydration of **3** with *p*-toluenesulfonic acid (PTSA) in chloroform gave, as expected, a compound less polar than **3** as shown by thin-layer chromatography (TLC). However, this compound proved to be of difficult isolation because the solvent removal led to the isolation of a polymeric material[6−8] containing only trace amounts of the expected **1**, as demonstrated by ^1H NMR spectroscopy. Conversely, when the dehydration was performed in $CDCl_3$, allowing the ^1H NMR analysis to be performed without the solvent elimination, a clear ^1H NMR spectrum compatible with the structure of **1** was obtained.

Thus, dehydration of **3** gave **1** which was stable in solution and polymerized upon solvent removal to give

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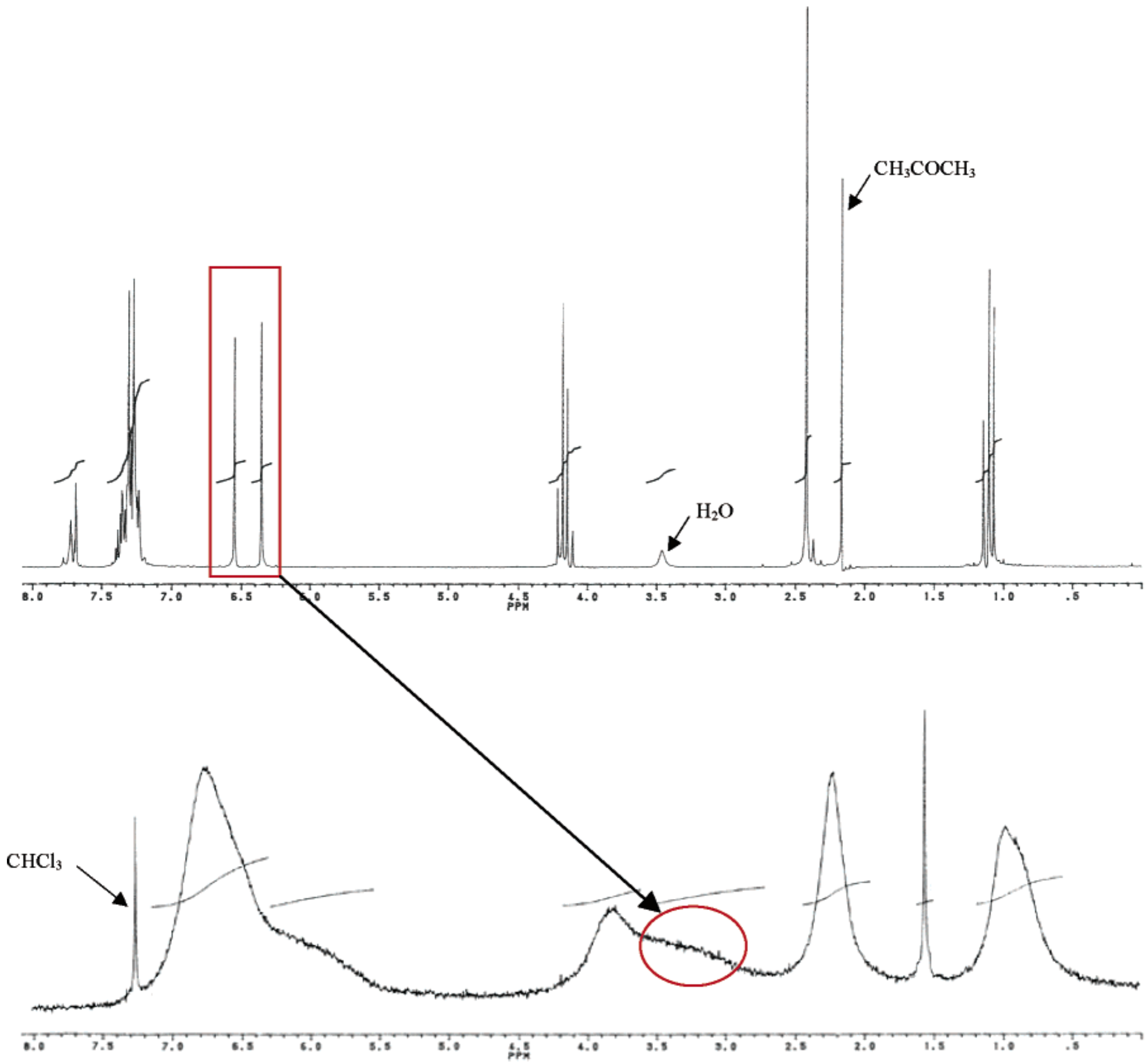

FIGURE 1. Comparison between the ^{1}H NMR spectra (200 MHz) of **BF1** (top) and of **poly-BF1** (bottom).

poly-BF1 showing distinct physicochemical characteristics. Indeed, the ^{1}H NMR spectrum of this material showed broad signals in place of the sharp ones typical of benzofulvene **1**. The signals attributable to the vinyl $=CH_2$ group of **1** (two singlets at 6.35 and 6.55 ppm) became a broad signal (centered at about 3.2 ppm) attributable to a $-CH_2-$ bridge in **poly-BF1** (Figure 1). The transformation of the vinyl $=CH_2$ group of **1** into a $-CH_2-$ bridge strongly support the polymer nature of **poly-BF1**.

The characterization of the freshly prepared material by a multiangle laser light scattering on-line to a size-exclusion chromatography (SEC-MALS) system gave a molar mass value extraordinarily high (approximately M_w = 2.5 million g/mol) and a dispersity index a little broader than 2 (D = 2.2) (Figure 2). Considering that the presence of aggregates was not observed in the freshly synthesized **poly-BF1**, this was a very interesting result. Both the intrinsic viscosity ([η] = 1.4 dL/g in THF) and the gyration radius (R_g = 58.9 nm) were consistent with the very high molar mass.

MALDI-TOF mass spectrometry of **poly-BF1** confirmed the polymeric nature of this material. The MALDI spectrum obtained with dithranol as the matrix (Figure 3) showed the presence of a series of peaks differing by 290 u (the molecular weight of monomer **1**) up to a mass-to-charge ratio of about 8000. Heavier polymeric species were undetectable under MALDI-TOF conditions.

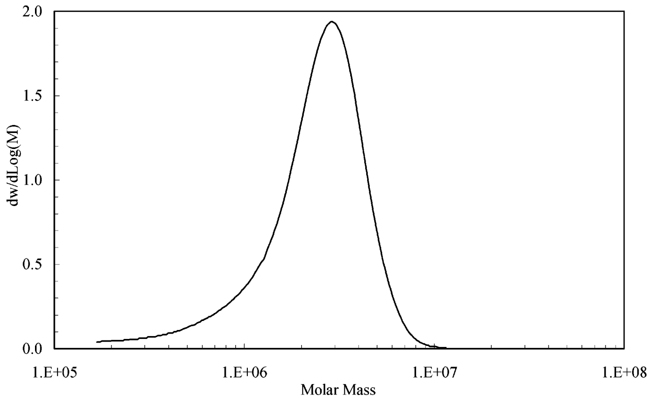

FIGURE 2. Differential molar mass distribution of **poly-BF1**.

In principle, *trans*-diene **1** can undergo either vinyl (1,2) or diene (1,4) polymerizations, each leading to

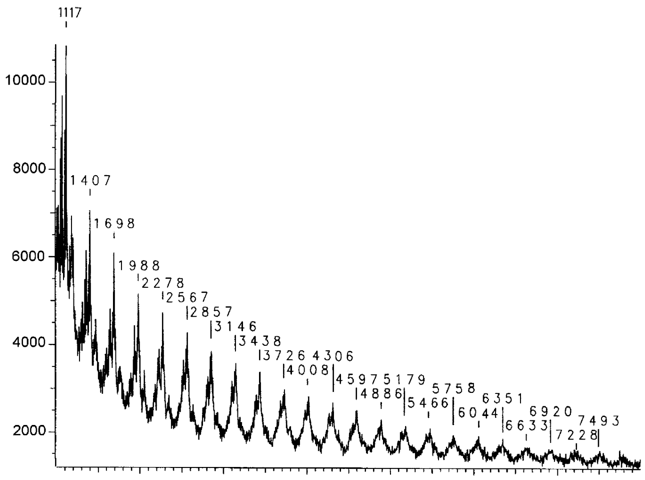

FIGURE 3. MALDI-TOF spectrum of **poly-BF1**.

different polymer backbones. The nature of the vinyl polymer of **poly-BF1** was suggested by the presence of two unusually shielded aromatic protons at about 6 ppm, consistent with the presence of strong interactions among the aromatic moieties (π-stacking). Indeed, preliminary molecular modeling studies indicated a higher degree of stacking in the assumed vinyl polymer with respect to the 1,4-enchained one. Moreover, 1,2-polymerization would preserve conjugation in the polymer between the donor aryl group and the acceptor ester group. However, 1,4-polymerization cannot be ruled out, and further studies are in progress in order to define the molecular structure of **poly-BF1** unambiguously.

Benzofulvene derivative **1** was stable in solution at reflux in the presence of a catalytic amount of dibenzoyl peroxide. Moreover, **poly-BF1** was obtained also in the case of the solvent elimination in the presence of a radical inhibitor such as 2,6-di-*tert*-butyl-*p*-cresol. These results suggest that free radical species are not involved in the polymerization mechanism, which would be ionic in nature. Again, the polymerization of **1** was active also in the absence of PTSA, suggesting cationic catalysis to be unnecessary. Probably, the solvent removal induces the strongly polarized[9] exocyclic double bonds of two molecules of **1** to interact with each other with the formation of a dimer featuring a zwitterionic tetramethylene moiety.[10] This zwitterionic intermediate would show a negative charge stabilized as an aromatic indenyl anion and an unstabilized CH_2^+ which could initiate the cationic polymerization process leading to **poly-BF1**. If this mechanism is operating, the presence of terminal charges can be assumed along with the reversibility of the polymerization process.

Heating the solutions of the polymer to reflux in aprotic solvents showing different boiling points (e.g., ethyl acetate, toluene, and xylene) led to both the depolymerization of **poly-BF1** and the regeneration of the fulvene monomer **1**. The fragmentation of the polymer was faster in xylene than in ethyl acetate. On the basis on these observations, the depolymerization process was followed by NMR spectroscopy at high temperature. Owing to the relatively low speed of the process at low temperatures, we chose to perform the experiments at different times in nitrobenzene at 140 °C. Figure 4 shows that the broad lines typical of the polymer progressively disappeared as a consequence of the exposure to high temperature to be replaced by the sharp signals of the fulvene monomer **1**. Thus, the restoring of the solvated conditions led the polymer to release the monomer at a temperature-dependent rate.

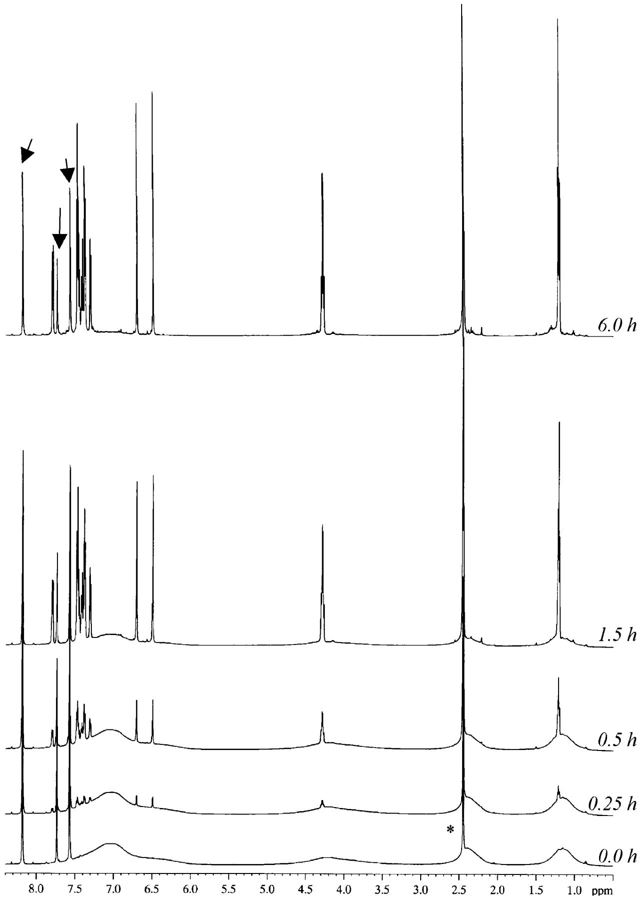

FIGURE 4. Thermal-induced depolymerization of **poly-BF1**, followed by ^1H NMR (600 MHz). Peak intensity of the spectra collected at 1.5 and 6.0 h were reduced by 25% and 50%, respectively. Arrows indicate the solvent (nitrobenzene) peaks. The asterisk indicates the water peak.

Finally, a significant change in the solubility of **poly-BF1** was observed after its prolonged storage as a solid. This suggests the possible formation of macromolecular aggregates or the increasing of the molecular weight by specific combination of the individual chains of **poly-BF1** in the solid state.

On the basis of these interesting properties, i.e., the high solubility in the most common organic solvents, and the susceptibility to molecular manipulation of **poly-BF1**, intriguing potential applications in synthesis can be envisioned, as well as in drug-controlled release, in the development of photoconducting and luminescent materials, in solid phase synthesis, and in catalysis, all of which will be suitably explored. As far as the application we have tested is concerned, we found that the polymer can be used as a stock form of benzofulvene derivative **1**. In

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fact, compound **1** generated from the polymer was used for the synthesis of spirocyclopropane derivative **4** by means of a palladium-catalyzed cyclopropanation[11] with diazomethane (Scheme 1).

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Supporting Information Available: Experimental details for the synthesis and the characterization of compounds **1**–**4** and **poly-BF1** (chemistry, NMR, MS, X-ray crystallography, SEC analysis). This material is available free of charge via the Internet at http://pubs.acs.org.

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