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Dibenzofulvene, a 1,1-Diphenylethylene Analogue, Gives a π-Stacked Polymer by Anionic, Free-Radical, and Cationic Catalysts

Tamaki Nakano,*[†,‡] Kazuyuki Takewaki,[‡] Tohru Yade,[‡] and Yoshio Okamoto[§]

PRESTO, Japan Science and Technology Corporation (JST)
Takayama-cho 8916-5, Ikoma, Nara 630-0101, Japan
Graduate School of Materials Science
Nara Institute of Science and Technology (NAIST)
Takayama-cho 8916-5, Ikoma, Nara 630-0101, Japan
Department of Applied Chemistry
Graduate School of Engineering, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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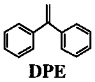
1,1-Diphenylethylene (**DPE**) is known as a representative vinyl compound that does not produce a homopolymer through any kind of catalysis, and its low reactivity has been ascribed to steric reasons.[1−3] Here we report that dibenzofulvene (**DBF**),[4] whose structure is closely related to that of **DPE,** affords a polymer by anionic, radical, and cationic catalyses. **DBF** differs from **DPE** only in the fact that the two phenyl groups are connected to each other to form a fused ring structure. In addition, the absorption and emission features of the polymerization products suggested that they possess a novel "π-stacked structure" in which the aromatic groups in the side chain are stacked on top of each other.


DBF


DPE

DBF was synthesized from 9-hydroxymethylfluorene (Aldrich) by the reaction in a methanol solution containing KOH according to the literature[5,6] and purified by recrystallization[7] from hexane (mp 50−52 °C (lit.[5] 48−49 °C)).

The conditions and results of the polymerization are summarized in Table 1. In the anionic polymerization, the reactions using *n*-butyllithium (*n*-BuLi) and 9-fluorenyllithium (FlLi) led to nearly complete monomer consumption at −78 °C, while that using CH_3MgBr required room temperature to achieve a 73% monomer conversion. It was interesting that *t*-BuOK, a weak nucleophile, very effectively polymerized **DBF** at −78 °C. In this case, generation of a 9-fluorenyl anion, a carbanion, from the oxy anion was indicated by the deep red color of the reaction mixture.[8] Cationic and free-radical polymerizations also produced a polymer. Under the reaction conditions shown in Table 1, **DPE** did not produce a polymer. In all cases, the products were only partially soluble in solvents such as tetrahydrofuran (THF) and chloroform. The ^{1}H NMR and MALDI-TOF mass analyses indicated that the THF-soluble parts have a vinyl polymer structure (Supporting Information).[9]

To obtain information on why **DBF** gives a polymer, while **DPE** does not, the electron density of the vinyl group was first considered. The ^{13}C chemical shift of the β-vinyl carbon of **DBF** was 107.7 ppm, while those of **DPE** and styrene were 114.3 and 113.6 ppm, respectively, as determined in $CDCl_3$ at 23 °C using a JEOL JNM-ECP600NK spectrometer (150 MHz), suggesting that the β-carbon of **DBF** has a higher electron density compared with those of **DPE** and styrene.[10] However, this only supports the reactivity of **DBF** during cationic polymerization. We next examined the structure of **DBF** using semiempirical molecular orbital calculations. The AM1 calculation[11] using the Hyperchem (Hypercube) software package suggested a nearly planar structure for **DBF** which is not possible for **DPE.** The nearly planar structure should not only reduce steric hindrance but also effectively stabilize the anionic, cationic, or radical species at the α-carbon through electron conjugation. In addition, the bond angle between the two vinyl-to-phenyl bonds in **DBF** was 105.6°, which is significantly deviated from 120°, implying that the vinyl group of **DBF** contains a significant strain energy. Therefore, strain relief may be a driving force of the **DBF** polymerization regardless of the type of active species. This would reasonably explain the fact that **DBF** polymerizes even with *t*-BuOK. The enhanced reactivity of cyclic monomers having an exomethylene group compared with the acyclic parent vinyl compound has been pointed out;[12,13] however, the acyclic counterparts do slowly produce homopolymers in the existing examples whereas **DPE** does not produce a homopolymer.

The absorption and emission spectra of the THF-soluble product of the anionic polymerization (run 2 in Table 1) along with those of fluorene as a model of the monomeric unit are shown in Figure 1. The THF-soluble part was purified by SEC fractionation and the chemical structure was identified as **1** (n = 3−17) by ^{1}H NMR and MALDI-TOF mass analyses. The absorption spectrum of the oligomers indicated a significant hypochromism and had the broader, red-shifted peaks compared with that of fluorene, suggesting that the side-chain fluorene groups are stacked and the chromophore-to-choromophore distance is short enough to cause a π−π interaction in the ground state. The degree of hypochromism is comparable to those reported for DNAs and oligomers having fully overlapped aromatic groups.[14−16] Furthermore, in the emission spectrum of the oligomers, the excimer band with a maximum at about 400 nm dominated over the monomer emission with negligible intensity whose wavelength corresponds to the emission band of fluorene. The emission spectrum of the oligomers was independent of concentrations below 1.3×10^{-5} M in fluorene units, indicating that the excimer is only formed intramolecularly. The excimer

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[†] PRESTO, JST.

[‡] Nara Institute of Science and Technology (NAIST).

[§] Nagoya University.

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(7) The monomer crystal changed into a polymeric product during storage, suggesting the possibility of a solid-state polymerization. This aspect will be reported elsewhere.

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(9) The IR spectra (Supporting Information) and elemental analysis indicated that the insoluble polymers have the same chemical structure as the soluble part. Because the anionic polymerization at [DBF]/[Li] = 5 under conditions similar to run 1 in Table 1 led to a higher content of THF-soluble part (47%), the insoluble polymers probably have higher molecular weights compared with the soluble parts.

(10) The Mulliken charges obtained by ab initio calculations supported this conclusion (Supporting Information).

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Table 1. Polymerization of Dibenzofulvene[a]

run	solvent	initiator	$[M]_0$ (M)	$[I]_0$ (M)	temp (°C)	time (h)	conv.[b] (%)	THF-insoluble part yield (%)	THF-soluble part yield (%)	Mn[d]
1	THF	*n*-BuLi	1.0	0.10	−78	24	>99	87	13	770
2	THF	9-FlLi	0.21	0.04	−78	24	>99	<1	>99	810
3	THF	CH_3MgBr	0.20	0.04	−78−rt[e]	96[e]	73	46	27	1650[f]
4	THF	*t*-BuOK	0.20	0.04	−78	24	>99	76	24	1170
5	CH_2Cl_2	BF_3-Et_2O	1.0	0.05	0	24	96	86	10	870
6	CH_2Cl_2	BF_3-Et_2O	1.0	0.20	rt	24	>99	82	17	1050
7	toulene	BPO-DMA[g]	0.88	0.048	0	24	22	15	7	2560[f,h]
8	toulene	AIBN	0.19	0.076	60	48	63	−	−	940[i]

[a] Monomer: 0.4−11.2mmol. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] THF-sol. part was a mixture of oligomers and unreacted monomer when the monomer conversion was not quantitative. The yield of this part was calculated excluding the weight of the unreacted monomer. [d] Determined by GPC using two TSKgel $\mathrm{G1000H_{HR}}$ columns connected in series with oligo(DBF)s as the standard (eluent, THF). [e] Reaction was performed first at −78 °C for 24 h and then at rt for an additional 72 h. Monomer conversion during the first stage at −78 °C for 24 h was 2%. [f] TSKgel $\mathrm{G6000H_{HR}}$ and $\mathrm{G3000H_{HR}}$ were used in a serial connection. [g] BPO = benzoyl peroxide. DMA = *N,N*-dimethylaniline. [h] Standard polystyrenes were used for calibration. [i] Obtained at 28% yield by fractionating $CHCl_3$-sol. part (yield 45%) of the crude mixture by preparative GPC using JAIGEL 1H and 2H columns connected in series (eluent, $CHCl_3$).

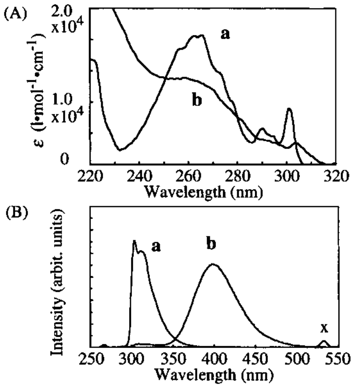
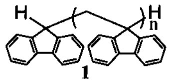


Figure 1. Absorption (A) and emission (B) spectra of fluorene (**a**) and oligo(DBF), **1** ($n = 3-17$) (**b**) in THF at ambient temperature (23 °C). The solution concentration for **a** was 1.14×10^{-5} M and that of **b** was 1.36×10^{-5} M (per monomeric residue). The excitation wavelength in B was 265 nm (a) and 267 nm (b).

emission is red-shifted compared with those of fluorene[17] (370 nm in toluene) and poly(2-vinylfluorene)[18] (380 nm in THF), suggesting that the excimer structure for poly(**DBF**) is somewhat different from those of fluorene and poly(2-vinylfluorene). These photophysical features suggest that the fluorene groups in the oligomers form a regular, stacked structure.

To obtain information on the polymer conformation, molecular mechanics and dynamics (MM and MD) calculations were performed with the Dreiding force fiel[19] (ver. 2.11) for a model trimer (**1**, $n = 2$) and a model decamer (**1**, $n = 9$) using the Cerius^2 (MSI) software package. For the model trimer, through the conformer search among the 1296 combinations of the four dihedral angles (Figure 2A) with the angle interval of 60°, the one shown in Figure 2B was found to be the most stable conformer. The structure of the conformer is characterized by the nearly all-trans, zigzag main chain and the fully overlapped neighboring fluorenyl groups. On the basis of this structure, an all-trans decamer was generated and optimized by the MM calculations to give the structure shown as Figure 2C. The stability of structure C was then assessed by the MD simulations. Structure C did not show any significant change in terms of the stacking of the fluorenyl groups through an MD simulation at 300 K for 5.2 ns. On the basis of a simulation at 600 K for 6.6 ns, structures D and E in Figure 2 were found in addition to structure C, the major conformation observed in the simulation. Structures D and E had ca. 10-kcal/mol higher steric energy than structure C. Hence, the conformation having an all-trans main-chain conformation such as Figure 2, B and C, is proposed for poly(**DBF**) as the most plausible structure with a possible conformational “mistake” at the chain terminals as in structures D and E.[20] Such a conformation is consistent with the observed photophysical features and is supported by the ^{1}H NMR spectra that indicates significant upfield shifts in the aromatic protons (Supporting Information).



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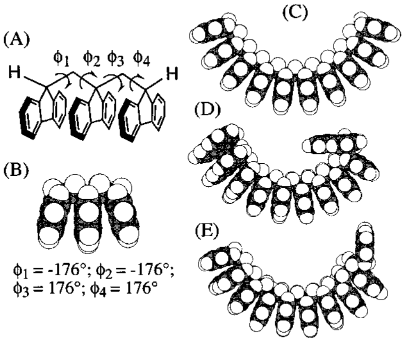

Figure 2. Structures of the model trimer with the definition of the dihedral angles (A), the most stable conformer for the trimer (B), a conformer of the model decamer constructed based on B and minimized by MM calculation (C), and the two conformations with the terminal fluorene unit being flipped generated in the MD simulation at 600 K (D, E).

In summary, this work revealed the unexpected, high polymerization activity of **DBF** and the unique conformation of the obtained polymer that may be recognized as a new structural motif of vinyl polymers. The $\pi-\pi$ interaction between the chromophores aligned along the polymer chain could realize some unprecedented photophysical and photoelectronic characteristics such as controlled energy and electron transfer, possibly leading to novel photoconducting and luminescent materials. Further studies on the detailed structure and photophysical aspects of the oligo(**DBF**)s are under way along with the design of novel π-stacked polymers.

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Supporting Information Available: Experimental procedures, compound characterization, details of molecular mechanics calculation, Mulliken charges of monomers, and IR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) MD simulations for an isotactic model of poly(2-vinylfluorene) indicated that π-stacking of the model was much less stable than that of the DBF decamer model (Supporting Information).