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Anionic Polymerization of a Benzofulvene Monomer Leading to a Thermoreversible π-Stacked Polymer. Studies in Macromolecular and Aggregate Structure

Andrea Cappelli,*,† Simone Galeazzi,† Germano Giuliani,† Maurizio Anzini,† Marianna Aggravi,‡ Alessandro Donati,‡ Lucia Zetta,§ Antonella Caterina Boccia,§ Raniero Mendichi,§ Gianluca Giorgi,|| Eugenio Paccagnini,⊥ and Salvatore Vomero†

Dipartimento Farmaco Chimico Tecnologico and European Research Centre for Drug Discovery and Development, Università degli Studi di Siena, Via A. Moro, 53100 Siena, Italy; Dipartimento di Scienze Chimiche e dei Biosistemi, Università degli Studi di Siena, Via A. Moro, 53100 Siena, Italy; Istituto per lo Studio delle Macromolecole (CNR), Via E. Bassini 15, 20133 Milano, Italy; Dipartimento di Chimica, Università di Siena, Via A. Moro, 53100 Siena, Italy; and Dipartimento di Biologia Evolutiva, Università degli Studi di Siena, Via A. Moro, 53100 Siena, Italy

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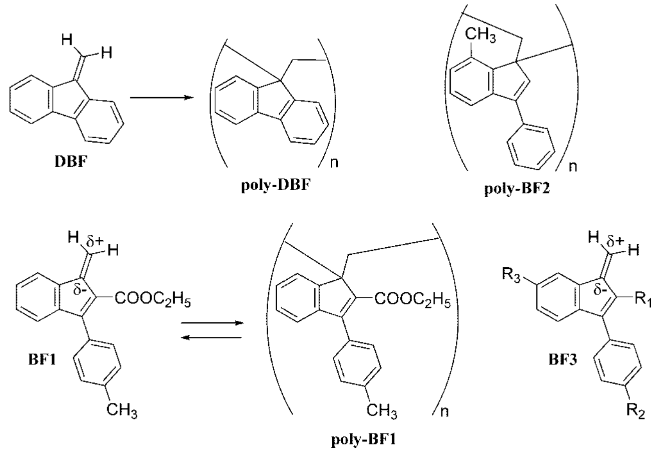
ABSTRACT: The polymerization of *trans*-diene **BF1** [ethyl 1-methylene-3-(4-methylphenyl)-1*H*-indene-2-carboxylate] has been studied in the presence of various amounts of an anionic initiator such as phenyllithium in order to obtain information on the properties of this diene monomer and on its polymers. The anionic polymerization of **BF1** produced a mixture of oligomers and a polymer (poly-**BF1-AP**), the proportion of which is regulated by the amount of the initiator used. Poly-**BF1** was separated from lower oligomers on the basis of the solubility in *n*-hexane, and the soluble material was further fractionated by chromatography to obtain activated monomers and dimers. The structure of dimers and poly-**BF1-AP** has been investigated by NMR spectroscopy, absorption and emission spectroscopy, and mass spectrometry. The whole set of results is consistent, confirming for poly-**BF1** a vinyl (1,2) polymer chaining stabilized by means of aromatic stacking interactions. The thermoreversibility of poly-**BF1-AP** was characterized by ^{1}H NMR and compared to its DSC features. Remarkably, SEC-MALS analysis showed that the molecular weight of poly-**BF1-AP** is relatively low (about 10 kg/mol), and SEM studies revealed that the polymer is liable to give nanospheres and microspheres showing favorable shapes and dimensions. These results suggest the potential tuning of the material properties of these π-stacked polymers by means of the regulation of the molecular weight.

1. Introduction

Fulvene is a cyclic isomer of benzene and one of the classical nonalternant π-electron systems, which has attracted much interest because of its potential tendency to fulfill the Huckel $4N + 2$ rule.[1,2] Fulvene is described to show zwitterionic character in its singlet ground state (S_0) and, in the opposite direction, in the lowest triplet state (T_1); thus, fulvene was claimed to act as an aromatic chameleon.[3] The dipolar structure is believed to result from intramolecular charge transfer from the exocyclic double bond to the five-member ring, which acquires a pseudoaromatic cyclopentadienide character. Substituents can affect to a variable extent the degree of the zwitterionic character. Electron-releasing groups in position 6 or electron-withdrawing groups on the ring reinforce the dipolar character, stabilize the fulvene, and reduce the tendency to oxygenation, dimerization, and polymerization. In fact, the dipole moment of fulvene is reported to be equal to 0.42 D and becomes 1.44 D in 6,6-dimethylfulvene and 4.5 D in 6-(dimethylamino)fulvene.[4,5] A survey of the literature showed that little information is available about the polymerization of fulvene derivatives (see for example refs 1 and 2).

Scheme 1



In dibenzofulvene (**DBF**, Scheme 1), the fulvene structure is integrated in a tricyclic system, which confers to the fulvene moiety some peculiar characteristics. For example, **DBF** polymerizes under a variety of conditions including anionic, cationic, and radical catalyzes to give poly-**DBF**, and the properties of polydibenzofulvene derivatives (e.g., poly-**DBF**) have been largely investigated.[6–12] For instance, poly-**DBF** is a new synthetic "π-way" molecule showing a hole drift mobility only slightly lower than that of Se,[13] an inorganic semiconductor, but it has been reported to show poor solubility and miscibility with other polymers.[6,7,11]

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* Corresponding author: Tel +39 0577 234320; Fax +39 0577 234333; e-mail: cappelli@unisi.it.

† Dipartimento Farmaco Chimico Tecnologico and European Research Centre for Drug Discovery and Development, Università degli Studi di Siena.

‡ Dipartimento di Scienze Chimiche e dei Biosistemi, Università degli Studi di Siena.

§ Istituto per lo Studio delle Macromolecole (CNR).

|| Università di Siena.

⊥ Dipartimento di Biologia Evolutiva, Università degli Studi di Siena.

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7-Methyl-1-methylene-3-phenylindene (**BF2**) is a benzofulvene derivative, which was described to polymerize under free radical catalysis to give a vinyl polymer containing pendant aromatic chromophores.[14]

We have recently reported that benzofulvene derivative **BF1** [ethyl 1-methylene-3-(4-methylphenyl)-1*H*-indene-2-carboxylate, Scheme 1] underwent spontaneous polymerization to give poly-**BF1**, a polymer characterized by a vinyl structure stabilized by aromatic stacking interactions and showing outstanding properties such as a thermoreversible polymerization/depolymerization, a susceptibility to molecular manipulation, and a high solubility in the most common organic solvents.[15,16]

Transmission electron microscopy (TEM) studies of poly-**BF1** revealed that this interesting polymer is liable to give nanostructured macromolecular aggregates.[16]

Moreover, a functionalized polymer structurally related to poly-**BF1** was shown to release the bioactive monomer (an angiotensin II AT_1 receptor antagonist) with a temperature-dependent kinetics until a temperature-dependent equilibrium is reached, as it occurs in equilibrium polymerization processes. The results of the binding studies performed on this polymer strongly support the exploration of the potentiality of the thermoreversible polymerization mechanism in controlled drug release from new polymeric prodrugs.[17]

In a previous paper we described the synthesis and the characterization of a series of benzofulvene derivatives **BF3** (related to **BF1**) showing spontaneous thermoreversible polymerization/depolymerization. The results obtained in the study demonstrated that most of the polymer properties (e.g., formation, molecular weight, structure, thermoreversibility, and aggregation into nanostructured entities) may be modulated by the stereoelectronic characteristics of the substituents present on the indene moiety.[18]

On the basis of the results obtained in the previous studies,[15–18] the properties of **BF1** and those of its polymers were more thoroughly investigated together with the role of the molecular weight distribution (MWD) on the aggregation properties (e.g., shape and dimensions of the nanoaggregates). Since spontaneous polymerization invariably gave very high molecular weight poly-**BF1**, the use of an anionic initiator such as phenyllithium (PhLi) was evaluated in order to obtain poly-**BF1** showing relatively low molecular weight. Moreover, by means of anionic polymerization, we expected to obtain **BF1** oligomers (e.g., **BF1** dimers) potentially useful as model molecules in the understanding of the poly-**BF1** structure by NMR spectroscopy.

This paper describes the results of a study focused on the synthesis and the characterization of low molecular weight polymers and oligomers of **BF1** obtained by polymerization in the presence of variable amounts of an anionic initiator such as PhLi.

2. Results and Discussion

2.1. Synthesis and Fractionation of Oligo- and Poly-BF1.

Since the spontaneous polymerization of *trans*-diene **BF1** occurs upon removal of the solvent, a 0.1 M solution of **BF1** in toluene was prepared as previously described[16] and then used in the anionic polymerization experiments without any particular purification procedure. The anionic polymerization experiments were performed in the presence of different stoichiometric ratios of PhLi (0.1, 0.5, and 1.0 equiv) at different reaction temperatures (−10, –50, and −98 °C; see Table 1). The reaction mixture was quenched by a careful addition of degassed acetic acid as protonating agent and, after the usual aqueous work-up, was fractioned on the basis of its solubility in *n*-hexane as the solvent.

Table 1. Anionic Polymerization of Benzofulvene Derivative BF1[a]

entry	initiator amount (equiv)	temp (°C)	*n*-hexane-soluble fraction yield (%)	*n*-hexane-insoluble fraction yield (%)
A	1	−98	85	15
B	1	−50	90	10
C	1	−50	94	6
D	1	−50	100	0
E	1	−10	97	3
F	1	−10	100	0
G	1	−10	100	0
H	0.5	−50	100	0
I	0.1	−50	15	85
J	0.1	−50	24	76

[a] The polymerization reaction was started by adding the appropriate amount of a commercial (1.8 M) solution of phenyllithium in dibutyl ether to 20 mL of a 0.1 M solution of **BF1** in toluene. Because of possible concentration variability of the commercial phenyllithium solution, the most significant runs were performed in duplicate or triplicate in order to evaluate the reliability of the results.

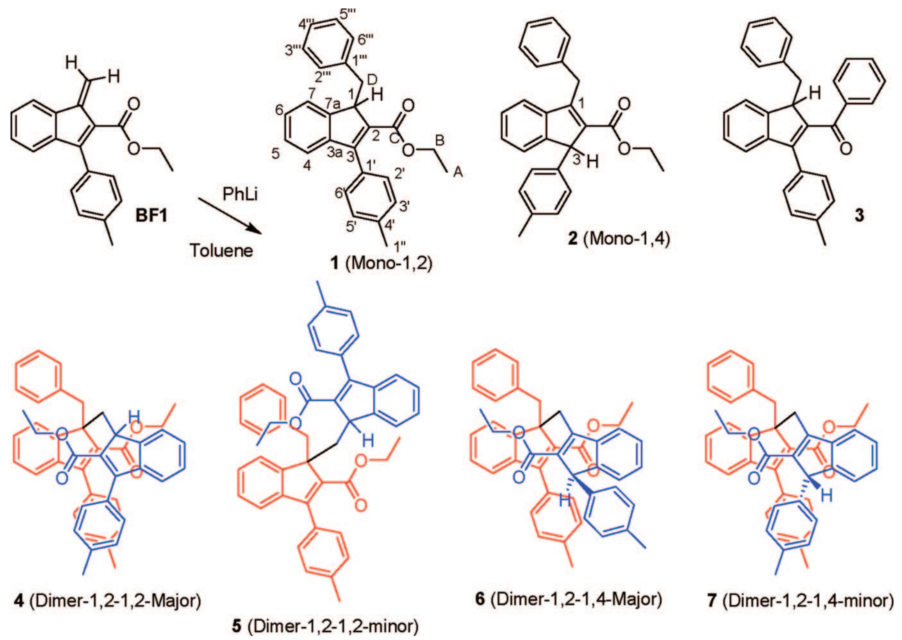
The experiments performed with a low stoichiometric ratio of the anionic initiator (e.g., 0.1 equiv) gave substantial amounts of insoluble polymeric fractions, while the use of an equivalent of PhLi led to small (or negligible) quantities of polymer and conspicuous fractions soluble in *n*-hexane.

The *n*-hexane-soluble fraction obtained from entry B (1 equiv of PhLi, −50 °C) was demonstrated to contain a complex mixture of low molecular weight poly-**BF1**. Direct-phase chromatography (e.g., flash chromatography) allowed the isolation of two activated monomer isomers (**Mono-1,2** and **Mono-1,4**, Scheme 2), of two pure activated dimer isomers (**Dimer-1,2–1,4-Major** and **Dimer-1,2–1,4-minor**), and of the mixture of two other dimers (**Dimer-1,2–1,2-Major** and **Dimer-1,2–1,2-minor**), which were separated by semipreparative reverse phase HPLC. Moreover, more polar fractions of the flash chromatography purification gave a complex mixture of low molecular weight poly-**BF1** (e.g., trimers and higher MW oligomers). The molecular weight distribution (MWD) of the *n*-hexane-insoluble polymeric fractions was characterized by a multiangle laser light scattering (MALS) photometer online to a size exclusion chromatography (SEC) system. The MWD of these poly-**BF1-AP** samples obtained by anionic polymerization was found to be very different (i.e., lower molecular weight, see below) from those of poly-**BF1** obtained by spontaneous polymerization (poly-**BF1-SP**).

These results suggest that *trans*-diene **BF1** polymerizes in the presence of an anionic initiator such as PhLi to give a polymer and/or oligomers in relation to the amount of the initiator employed. In particular, stoichiometric amounts of PhLi produced almost exclusively soluble oligomers, while practically no insoluble polymeric fraction were found (Table 1). Low initiator amounts (i.e., 0.1 equiv) led to the presence of both oligomers and a substantial amount of poly-**BF1** in the reaction mixture.

The comparison of the HPLC-MS chromatograms (data not shown) of the *n*-hexane-soluble fractions obtained in the experiments shown in Table 1 suggests that the dimeric species appear to be among the major oligomers independently of the reaction temperature. This result suggests that the conditions of the anionic polymerization lead to an equilibrium among various oligomers in which dimers are the most stable species formed. The equilibrium could be similar to that shown by **BF1** in the presence of *N*-methylpiperazine[16] with the difference that the anionic activated monomer is capable of starting the propagation step leading to poly-**BF1**, which becomes the major species when low stoichiometric ratios of PhLi are used (entries I and J of Table 1).

Scheme 2[a]



[a] In dimers **4–7** the red structures refer to the *bf1* moiety and the blue ones to the *bf2* one.

Table 2. Summary of Results Obtained with Five Poly-BF1 Samples: Two from Anionic Polymerization and Three from Spontaneous Polymerization

sample	polymerization	M_w (kg/mol)	M_p (kg/mol)	D
poly-**BF1-AP** (entry I)	anionic	12.2	13.9	2.1
poly-**BF1-AP** (entry J)	anionic	7.4	8.2	2.0
poly-**BF1-SP** (P100)	spontaneous	867	955	2.0
poly-**BF1-SP** (P200)	spontaneous	1605	1870	1.9
poly-**BF1-SP** (P400)	spontaneous	2670	2950	2.0

The particular stability of the activated dimer can represent an indirect evidence of the role of the postulated zwitterionic dimer in the spontaneous polymerization of **BF1**.[16]

2.2. Molecular Weight Distribution Characterization. The molecular weight distribution (MWD) characterization of the freshly prepared poly-**BF1** was performed by means of a SEC-MALS system. Table 2 summarizes the most important data for five poly-**BF1** samples: two samples obtained by anionic polymerization (entries I and J of Table 1) and, only by way of comparison, three samples obtained by spontaneous polymerization with different amounts of the monomer in the starting solution.[16] These results clearly show that the M_w average of poly-**BF1-AP** (this study) was relatively low and very different from the M_w average of the poly-**BF1-SP** samples. Specifically, for the two preparations, I and J, the M_w average was 12.2 and 7.4 kg/mol, respectively. The little difference in MWD shown by the two poly-**BF1-AP** samples (shift in molecular weight of about 5 kg/mol) is probably due to both the concentration variability of the commercial phenyllithium solution and the experimental uncertainty. The dispersity index $D = M_w/M_n$ (where M_n denotes the numeric-average of the molar mass) of these two poly-**BF1-AP** samples was ~2. Previous studies[15,16] demonstrated that the M_w average of poly-**BF1** samples obtained by spontaneous polymerization, ranging from about 870 to 2700 kg/mol, was affected by the amount of the monomer in the starting solution. The present study demonstrates that the presence of a significant polymeric fraction and the M_w average of poly-**BF1-AP** samples substantially depends on the amount of the PhLi initiator used.

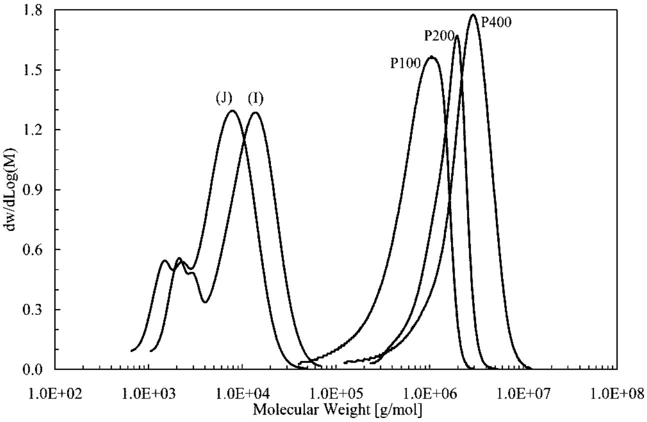


Figure 1. Comparison between the differential MWD, from SEC-MALS, of two poly-**BF1** samples (entries I and J of Table 1) by anionic polymerization and three poly-**BF1** samples (P100, P200, and P400) by spontaneous polymerization.

The previous considerations are confirmed by an accurate analysis of the whole MWD. Figure 1 shows the comparison of the differential MWD, from SEC-MALS, of poly-**BF1** samples from both anionic and spontaneous polymerization methods. The lowest MWD poly-**BF1** samples are the ones obtained by anionic polymerization (entries I and J, Table 1). On the other hand, the highest MWD poly-**BF1** samples (P100, P200, and P400, where the number after P indicates the mg of monomer used in the synthesis, see ref 16) are from spontaneous polymerization. It is noteworthy that very different MWD results were obtained when two different polymerization methods were used.

The accurate analysis of the MWD of the two poly-**BF1-AP** samples showed, beside the polymeric main peak ($M_p = 13.9$ kg/mol for entry I and 8.2 kg/mol for entry J, where M_p denotes the peak molecular weight), the presence of some other minor oligomeric peaks. In other words, the *n*-hexane-insoluble poly-**BF1** fraction contains some *n*-hexane-insoluble oligomers. Approximately, the molecular weight of these insoluble oligomers is 1800 g/mol (probably **6BF1·C_6H_6**) and 2900 g/mol (probably **10BF1·C_6H_6**).

2.3. Structure of Dimers 4–7 and Poly-BF1. *2.3.1. NMR.* The ^{1}H and ^{13}C NMR spectra of dimers **4–7** were assigned by means

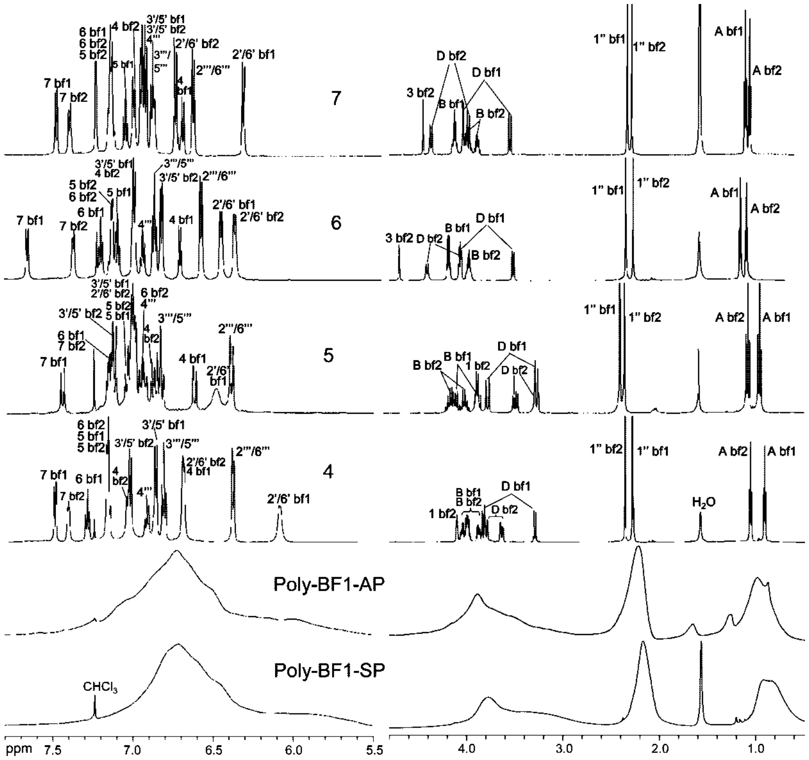


Figure 2. Comparison of the ^{1}H NMR spectra of dimers **5** (400 MHz, CDCl$_3$), **4**, **6**, **7**, poly-**BF1-AP,** and poly-**BF1-SP** (600 MHz, CDCl$_3$).

of correlation spectroscopy (COSY), nuclear Overhauser effect spectroscopy (NOESY), heteronuclear single quantum coherence (HSQC), and heteronuclear multiple bond connectivity (HMBC) experiments; the assigned ^{1}H and ^{13}C NMR spectra are reported in Figures 2 and 3, respectively.

The single benzyl ring, deriving from the PhLi initiator, was used as the entry point in the strategy of spectral assignment, being an AA′XX′Y NMR system, namely a doublet of intensity two (2‴/6‴) and two triplets of intensity one (4‴) and two (3‴/5‴), respectively. The COSY spectrum confirmed the correlations. The remaining aromatic rings are couples of the AA′XX′ or ABCD spin systems for the 4-methylphenyl and the indene rings, respectively. The NOESY dipolar interaction between the benzyl 2‴/6‴ protons and D-*bf1*, allowed to distinguish protons D of the two monomers. In dimers **4** and **5** D-*bf1* is always an AB system while protons D-*bf2* belong to an ABX system, where X is H-1; in **6** and **7** both D-*bf1* and D-*bf2* belong to AB systems, C-1 being quaternary. This feature allows us to assign 1,2 or 1,4 enchainment directly from the proton NMR spectrum.

NOE correlations between protons D of each monomeric unit and the corresponding proton 7 of the same unit, together with HMBC correlations within the indene protons and between the indene and the 4-methylphenyl protons, allowed to unambiguously assign *bf1* and *bf2* of each dimer.

The key information provided by the analysis of the chemical shift values and NOESY spectra of dimers **4, 6**, and **7** is the tendency to accommodate their bicyclic moiety in an antiparallel stacked orientation (Scheme 2). This observation is very important in the case of major 1,2–1,2-dimer **4** in which the tetrahedral geometry of both the indene C-1 atoms forces the indene moieties to stay closely stacked and the pendent phenyl groups appear to interact with the six-member ring of the indene nucleus (or with each other) by means T-shaped aromatic–aromatic interactions (see Supporting Information). This assumption is supported by the comparison of the chemical shifts (δ) and NOESY contacts for major (**4**) and minor (**5**) isomers of the 1,2–1,2 dimer.

The chemical shift analysis shows the following evidence: (a) 2′/6′-*bf*1 protons of both species **4** and **5** are upfield shifted with respect to the corresponding 2′/6′-*bf*2 protons, indicating that the benzyl group linked to *bf*1 induced a shielding effect on these protons owing to magnetic anisotropy. (b) H-2′/6′-*bf*1 and H-2′/6′-*bf*2 of major species **4** are strongly upfield shifted (0.45 and 0.32 ppm, respectively) with respect to the corresponding H-2′/6′-*bf*1 and H-2′/6′-*bf*2 of minor **5**, indicating these protons of **4** were affected by an additional shielding field, owing to magnetic anisotropy of the indene ring. (c) The chemical shift values of 3′/5′-*bf*1 and 3′/5′-*bf*2 protons of **4** are less affected (0.15 and 0.10 ppm respectively) by this shielding effect (with respect to the corresponding **5** protons) because of their distal position from the indene ring and benzyl anisotropic cones.

In the NOESY spectrum of **4**, the cross-peaks observed for the methyl protons of the ethyl group are diagnostic. In fact, A-*bf*1 and A-*bf*2 protons show symmetric intra- and inter-residue cross-peaks. Namely, H-A-*bf*1 is connected with both H-2′/6′-*bf*1 and H-3′/5′-*bf*1 (intra-residue) and with H-6-*bf*2 and H-7-*bf*2 (inter-residue) and H-A-*bf*2 is connected with H-2′/6′-*bf*2 and H-3′/5′-*bf*2 (intra-residue) and with H-6-*bf*1 and H-7-*bf*1(inter-residue).

These observations confirm the hypothesis of an antiparallel stacked orientation of indene moieties of **4** with a further stabilization due to "symmetric" (pendant) phenyl–indene interactions.

On the other hand, the NOESY spectrum of dimer **5** is characterized by the interaction between H-1-*bf2* and H-7-*bf1* and the absence of dipolar interactions between ester CH$_2$–CH$_3$ and the indene hydrogen atoms. These results suggests for dimer **5** a peculiar arrangement of the two benzofulvene units due to the "isotactic configuration".

The different samples of poly-**BF1** obtained by anionic polymerization were studied by NMR spectroscopy in comparison with a standard sample obtained by spontaneous polymerization (poly-**BF1-SP**). The ^{13}C NMR spectra of the samples of poly-**BF1-AP** from entries I and J (Table 1) were practically indistinguishable. The assignment reported in Figure

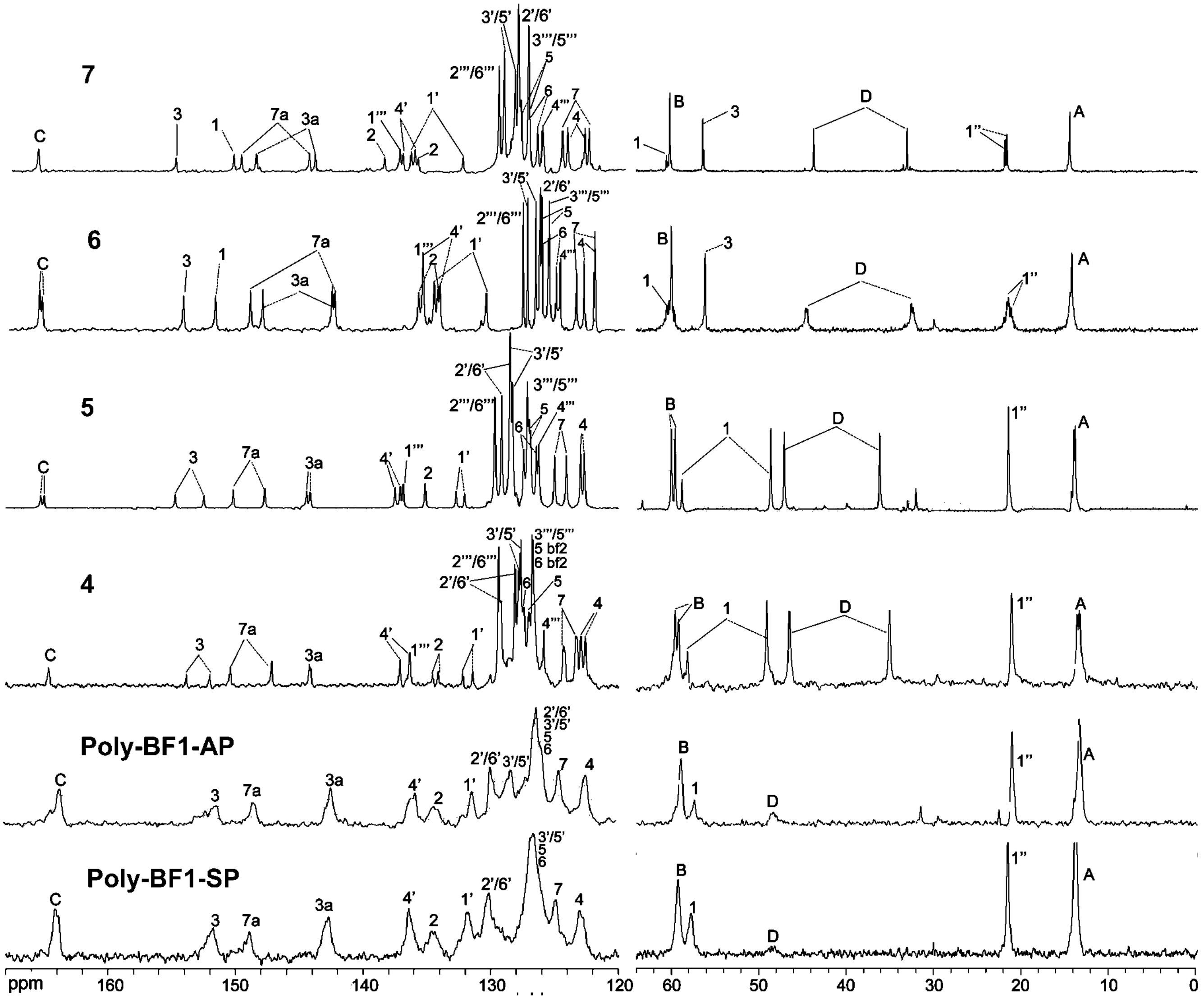


Figure 3. Comparison of the ^{13}C NMR (CDCl$_3$) spectra of dimers **4–7**, poly-**BF1-AP**, and poly-**BF1-SP**. In the spectra of dimers **4–7**, solid lines indicate the signals attributable to the *bf1* moiety of dimers, while dashed lines refer to the *bf2* moiety; when this distinction is not indicated, signals are overlapped.

3 was performed by integrating the direct evidence (from HMBC and HSQC spectra) with the information obtained from the ^{13}C NMR spectra of dimers **4–7**.

The comparison of the ^{13}C NMR spectra (Figure 3) obtained in CDCl$_3$ showed that polymerization of **BF1** in the presence of PhLi as an anionic initiator gave a polymer showing NMR features very similar to those shown by poly-**BF1-SP**. The main difference is the apparent intensity decrease of the signal at 129.9 ppm (attributed to C-2′/6′) and the appearance of a new signal at 128.3 ppm (attributed to a second component of C-3′/5′) in the spectrum of poly-**BF1-AP**. Moreover, a more limited splitting was observed for the signal at 136.1 ppm of poly-**BF1-SP** (attributed to C-4′), which becomes definitely splitted into two signals in the spectrum of poly-**BF1-AP** (135.7 and 136.1 ppm). It is noteworthy that the signal at 135.7 ppm is as sharp as the one at 129.9 ppm, while the others at 136.1 and 128.3 ppm are relatively broad. These observations suggest the possible existence of isomers of poly-**BF1-AP** showing differences in the environment of the pendent phenyl group. A similar behavior is absent in poly-**BF1-SP**.

The comparison of the ^{13}C NMR spectra of poly-**BF1** with those of dimers **4–7**, and in particular the similarities between the spectra of dimers **4** and **5** and those of poly-**BF1** confirm again the vinyl nature of this polymer. Finally, the comparison

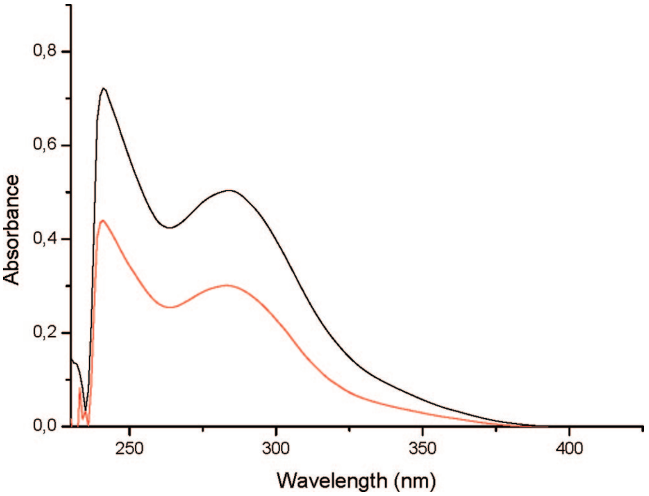


Figure 4. Comparison of the absorption spectra of poly-**BF1-AP** (black) and poly-**BF1-SP** (red). The spectra were obtained in chloroform at room temperature. The concentrations in monomer base unit were ca. 4.3 × 10^{-5} mol/L (poly-**BF1-AP**, entry I) and 2.6 × 10^{-5} mol/L (poly-**BF1-SP**, P400).

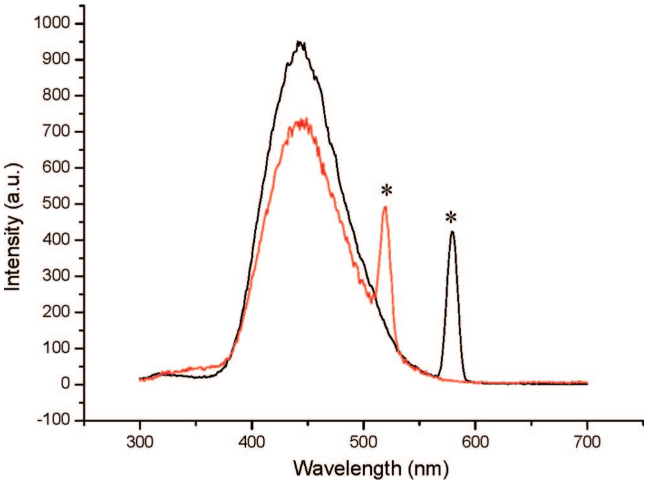


Figure 5. Comparison of the emission spectra of poly-**BF1-AP** (black) and poly-**BF1-SP** (red). The spectra were obtained in chloroform at room temperature. The excitation wavelengths were 288 nm (poly-**BF1-AP**, entry I) and 258 nm (poly-**BF1-SP**, P400). The asterisks indicate the secondary scattering of the excitation beam.

of ^{1}H NMR spectra of poly-**BF1-AP** with those of dimers **4–7** (Figure 2) suggests that dimer **4** can be considered a good candidate as the dimeric unit of this polymer.

2.3.2. Absorption and Emission Spectroscopy. The absorption and emission spectra of poly-**BF1-AP** are practically indistinguishable from those of poly-**BF1-SP** (Figures 4 and 5). This result suggests a similar extent of the π-stacking interactions among the aromatic moieties.

2.3.3. Mass Spectrometry. The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra obtained with the two samples of poly-**BF1-AP** (Figure 6) confirmed the structure of this polymer. In fact, they showed the presence of a series of peaks differing by 290 u (the molecular weight of monomer **BF1**) up to a mass-to-charge ratio of about 6500. As previously observed for poly-**BF1-SP**, heavier polymeric species were undetectable under MALDI-TOF conditions.

2.3.4. Differential Scanning Calorimetry. The two most significant samples of poly-**BF1-AP** (entries I and J of Table 1) were characterized by differential scanning calorimetry (DSC) over a temperature range of 40–340 °C at a heating rate of 20 °C/min for the identification of potential solid-state changes. DSC analysis showed an endothermic peak broader (Figure 7) than that of poly-**BF1-SP**.[18]

The comparison of the previously published DSC curve[18] of poly-**BF1-SP** with its DTGA (differential thermogravimetric analysis) plot[16] suggests the existence of a relationship between the DSC endothermic peak at 235 °C and the DTGA peak at 240–250 °C. Thus, the endothermic peak in the DSC trace can be attributed to the depolymerization process.[18] Moreover, in previously described poly-**BF3** series, a relationship seems to exist between the DSC curve and the thermoinduced depolymerization in nitrobenzene at 150 °C. In fact, in the polymers showing a sharp peak (characterized by an high ΔH value) in their DSC curve, the depolymerization is almost complete after 3–6 h heating.[18] On the other hand, the polymers showing an apparent equilibrium of the thermoinduced depolymerization in nitrobenzene at 150 °C are characterized by broad DSC peaks.[18] The data shown in Table 3 suggest that poly-**BF1-AP** belongs to the latter category, but the detailed rationalization of the relationships among the molecular weight, DSC features, and the depolymerization behavior is far from obvious.

2.4. Thermoreversibility Analysis. Thermoinduced depolymerization of poly-**BF1-AP** was followed by ^{1}H NMR spectroscopy. A solution of 5.0 mg of poly-**BF1-AP** in 0.5 mL of nitrobenzene-d_5 was heated at 150 °C, and ^{1}H NMR spectra were recorded at regular time intervals. In order to appreciate the variation in monomer concentration, the signals attributable to vinylene group were integrated, and the integral values were compared to that of the lowest field signal of nondeuterated nitrobenzene, which was considered as an internal standard. Figure 8 suggests for poly-**BF-AP** a thermoinduced depolymerization behavior similar to that shown by poly-**BF1** obtained by spontaneous polymerization, but the reaction seemed to reach an apparent equilibrium after 24 h heating, whereas an almost complete depolymerization was observed for poly-**BF1-SP** after 3–6 h heating in nitrobenzene at 150 °C.[18] The apparent equilibrium reached by poly-**BF1-AP** may be explained in terms of the equivalence in the depolymerization and repolymerization rates (reversible polymerization), but also with the possible presence of "imperfections" (i.e., structural differences with respect to poly-**BF1-SP**) in the polymer chains capable of slowing down the depolymerization process. The existence of these "imperfections" is suggested by the comparison of the ^{13}C NMR spectra of the two polymer types (Figure 3). Thus, further experiments were performed with poly-**BF1-AP** in order to better characterize the features of the depolymerization process.

Poly-**BF1-AP** is terminated at both chain ends: one end bears the phenyl group of the anionic initiator, which is likely to be fixed, while the other end is characterized by the presence of a relatively acidic proton linked to the indenyl moiety. If the propagation/depropagation reaction requires the presence of a negative charge in the terminal indenyl moiety, the reaction kinetics will depend on the concentration of the deprotonated chains and ultimately on the acid–base equilibrium. In deuterated nitrobenzene, the depolymerization rate is negligible at room temperature probably because of the low amount of the deprotonated chain, while it increases with temperature probably because of the increase in proton mobility. In these conditions, repolymerization of **BF1** on cooling is expected to be a very slow process, and spontaneous polymerization usually occurs at concentration values (e.g., $>$0.4 M in chloroform at room temperature) higher than that used in the thermoinduced depolymerization experiments.

^{1}H NMR depolymerization experiments with a solution of poly-**BF1-AP** (entry I, 5.0 mg) in C_6D_6 (0.5 mL) in the presence and in the absence of a base such as DBU (0.25 or 0.50 μL) show that depolymerization at room temperature is negligible in the absence of DBU, while it is significant in the presence of the base. At room temperature an apparent equilibrium is reached after 5–6 days in the presence of DBU (0.25 μL). The apparent equilibrium is characterized by the presence of a prominent amount of polymer with respect to the formed monomer. The depolymerization rate increases at 60 °C, and an apparent equilibrium is reached after 6–9 h. A rough estimate of the monomer concentration at the apparent equilibrium at different temperatures supports the reversible nature of poly-**BF1-AP** depolymerization, but further studies are needed for a detailed understanding of the differences between poly-**BF1-AP** and poly-**BF1-SP**.

2.5. Aggregate Structure. A sample of poly-**BF1-AP** (entry J, M_w = 7.4 kg/mol) was dissolved in dichloromethane and precipitated in the excess of a bad solvent (ethanol), collected by filtration, dried under reduced pressure, and finally observed by scanning electron microscopy (SEM) after sputter-coating with gold. The comparison of the images obtained (Figure 9, top) with those obtained with poly-**BF1-SP** (Figure 9, bottom; see ref 18) shows a different aggregation behavior, possibly related to the difference in the molecular weights. In fact, the polymer obtained by anionic polymerization appears to be liable to give nanospheres and microspheres showing favorable shapes

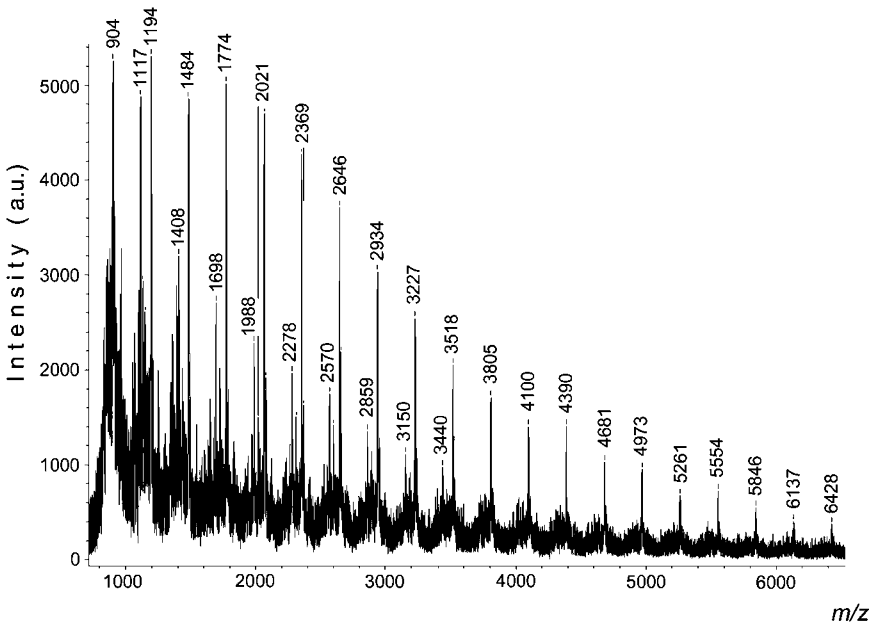


Figure 6. MALDI-TOF spectrum of poly-**BF1-AP** (entry J).

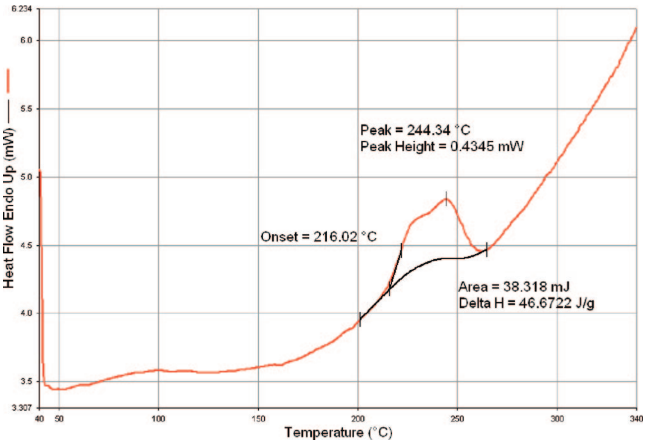


Figure 7. DSC curve of poly-**BF1-AP** (entry I).

and dimensions. On the other hand, poly-**BF1-SP** has the propensity to generate complex aggregates, which are related to those previously observed by transmission electron microscopy (TEM).[18]

3. Conclusions

The results of the work described herein demonstrate that *trans*-diene **BF1** is capable of polymerizing in the presence of an anionic initiator such as PhLi to give a polymer and/or oligomers in relation to the amount of the initiator employed. In particular, stoichiometric amounts of PhLi produce almost exclusively *n*-hexane-soluble oligomers, whereas low initiator amounts lead to the presence of both oligomers and a substantial amount of poly-**BF1-AP** in the reaction mixture.

The fractionation of the *n*-hexane-soluble material led to the isolation of two monomeric species (**1** and **2**) and four dimeric species **4–7**, which were studied by NMR spectroscopy. The molecular structures of the activated monomer isomers and of the four dimeric species isolated suggest that **BF1** reacts with PhLi to give activated monomer **1** (in the anionic form) capable of interacting with another molecule of **BF1** to give the anionic form of dimer **4**, which may play the role of growing intermediate in the formation of poly-**BF1-AP**. Moreover, the anions of **1** and **4** can undergo isomerization (double bond shift) into anions of **2** and **6**, respectively, which are less available as growing intermediates because of steric reasons. The events originate a polymerization equilibrium in which the dimers appear to be the most stable species formed when 1 equiv of PhLi is used, and poly-**BF1-AP** is the major species when lower initiator amounts are employed.

SEC-MALS analysis demonstrates that the molecular weight distribution of poly-**BF1** obtained by anionic polymerization is characterized by a significantly lower molecular weight with respect to those shown by poly-**BF1** obtained by spontaneous polymerization. However, the higher molecular weight with respect to the value calculated from the initiator amount may be related to the existence of equilibrium among the various activated oligomers, which lowers the number of the growing intermediates.

NMR spectroscopy shows that the anionic polymerization of **BF1** gives a poly-**BF1** exhibiting NMR features very similar to those shown by the polymer obtained by spontaneous polymerization (poly-**BF1-SP**). The observed differences involve ^{13}C NMR signals attributable to carbon atoms belonging to the pendent phenyl group and may be related to a different tacticity.

The stringent similarity of poly-**BF1-AP** electronic spectra (absorption and emission) with the corresponding ones of poly-**BF1-SP** supports a similar extent of the π-stacking interactions among the aromatic moieties in these differently prepared polymer.

Moreover, the mass spectrometry characterization by MALDI-TOF confirmed the structural features of poly-**BF1-AP**.

The thermoreversibility analysis of poly-**BF1-AP** shows different features of the depolymerization process with respect to the results obtained with poly-**BF1-SP**. These differences in the depolymerization of poly-**BF1-AP** are anticipated by the different DSC features and are likely to be due to the phenyl capping at one end of the polymer chain and/or to the structural differences with respect to poly-**BF1-SP**.

Finally, scanning electron microscopy studies performed with the polymers obtained by the two different polymerization methods show a different aggregation behavior possibly related to the difference in the molecular weight. In fact, poly-**BF1-AP** (lower molecular weight) shows the tendency to aggregate in nanospheres and microspheres, while poly-**BF1-SP** (high molecular weight) tends to generate larger fractal-like ag-

Table 3. Comparison of Some Significant DSC Features of the Studied Polymers with the Molecular Weight and the Thermoinduced Depolymerization Followed by ^{1}H NMR Spectroscopy

sample	polymerization	M_w (kg/mol)	peaks no. (appearance)	temp (°C)	ΔH (J/g)	thermoinduced depolymerization at 150 °C by ^{1}H NMR
poly-**BF1-AP** (entry I)	anionic	12.2	1 (broad)	228–244	46.7	equilibrium after 24 h
poly-**BF1-AP** (entry J)	anionic	7.4	1 (broad)	222–239	37.7	equilibrium after 24 h
poly-**BF1-SP** (P400)	spontaneous	2670	1 (sharp)	235	94.3	depolymerization almost complete after 3–6 h

gregates.[18] Since nanospheres, microspheres, and nanoporous materials can be of interest in controlled drug release and in several other fields of materials science, the results obtained in the present study can be considered very promising as suggest the potential tuning of the material properties of these π-stacked polymers by means of the regulation of their molecular weight.

Figure 8. Thermoinduced depolymerization of poly-**BF1-AP** (entry I), followed by ^{1}H NMR (400 MHz). A solution of 5.0 mg of poly-**BF1** in 0.5 mL of nitrobenzene-d_5 was heated at 150 °C, and ^{1}H NMR spectra were recorded at regular time intervals. In order to appreciate the variation in monomer concentration, the signals attributable to vinylene group were integrated, and the integral values were compared with that of the lowest field signal of nondeuterated nitrobenzene, which was considered as an internal standard. Integrals are omitted in the figure for the sake of clarity. The arrows indicate the solvent peaks, and the closed circle indicates the water peak.

4. Experimental Section

Synthesis. Melting points were determined in open capillaries in a Gallenkamp apparatus and are uncorrected. UV/vis spectra were recorded with a Shimadzu 260 spectrophotometer, and the emission spectra were performed by means of a Shimadzu RF-5001PC instrument. Merck silica gel 60 (230–400 mesh) was used for column chromatography. Merck TLC plates with silica gel 60 F254 were used for TLC. ^{1}H NMR spectra were recorded at 200 MHz (Bruker AC200 spectrometer), at 400 MHz (Bruker DRX-400 AVANCE spectrometer), or at 600 MHz (Bruker DRX-600 AVANCE spectrometer) in the indicated solvents (TMS as internal standard): the values of the chemical shifts are expressed in ppm and the coupling constants (J) in Hz.

Procedure for the Preparation of Solutions of Ethyl 1-Methylene-3-(4-methylphenyl)-1*H*-indene-2-carboxylate (BF1) in Toluene. A mixture of ethyl 1-hydroxy-1-methyl-3-(4-methylphenyl)-1*H*-indene-2-carboxylate[15] (5.0 g, 16 mmol) in toluene (160 mL) with a catalytic amount of *p*-toluenesulfonic acid monohydrate (PTSA) (0.61 mg, 3.2 mmol) was heated under reflux for 25 min and cooled to room temperature. The reaction mixture was washed with a saturated solution of $NaHCO_3$ and dried over sodium sulfate to afford a stock (about 0.1 M) solution of **BF1**, which was stored under an argon atmosphere. MS(ESI): *m/z* 313 $[M + 23]^+$, 291 $[M + 1]^+$.

Polymerization of BF1 in the Presence of Phenyllithium. The solution of **BF1** (ca. 0.1 M in toluene, 20 mL, ca. 2 mmol) in a round-bottomed flask was degassed with an argon stream and cooled to the suitable temperature. To the solution was added the appropriate amount of commercial (1.8 M, Aldrich) solution of phenyllithium in dibutyl ether, and the reaction mixture was stirred at the same temperature for 20 min. The resulting mixture was then quenched by a careful addition of degassed acetic acid, washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The resulting residue was treated with *n*-hexane (30 mL) and stirred at room temperature for 4 h. The insoluble material was collected by filtration and dried under reduced pressure to give the *n*-hexane-insoluble fraction (Table 1). The filtrate was concentrated under reduced pressure to give a viscous oil residue which constituted the *n*-hexane-soluble fraction (Table 1).

Ethyl 1-Benzyl-3-(4-methylphenyl)-1*H*-indene-2-carboxylate (1). Positional isomer **1** of activated monomer (**BF1·C$_6$H$_6$**) was isolated by flash chromatography of the *n*-hexane-soluble fraction of entry B (Table 1) with *n*-hexane−dichloromethane (6:4) as the eluent to obtain 0.030 g (yield 4%) of **1** as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): 1.15 (t, $J = 7.1$, 3H), 2.38 (s, 3H), 3.01 (dd, $J = 13.0$, 8.1, 1H), 3.59 (dd, $J = 13.1$, 4.0, 1H), 4.17 (m, 3H), 6.99 (m, 2H), 7.09–7.28 (m, 11H). MS (ESI): *m/z* 391 $[M + 23]^+$.

Ethyl 3-Benzyl-1-(4-methylphenyl)-1*H*-indene-2-carboxylate (2). Positional isomer **2** of activated monomer (**BF1·C$_6$H$_6$**) was isolated by flash chromatography of the *n*-hexane-soluble fraction of entry B (Table 1) with *n*-hexane−dichloromethane (6:4) as the eluent to obtain 0.049 g (yield 7%) of **2** as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): 1.10 (t, $J = 7.3$, 3H), 2.27 (s, 3H), 4.12 (m, 2H), 4.42 (d, $J = 14.6$, 1H), 4.56 (d, $J = 14.3$, 1H), 4.89 (s, 1H), 6.98 (m, 4H), 7.13–7.44 (m, 9H). MS (ESI): *m/z* 391 $[M + 23]^+$.

[1-Benzyl-3-(4-methylphenyl)-1*H*-inden-2-yl](phenyl)methanone (3). The title compound was isolated by flash chromatography of the *n*-hexane-soluble fraction of entry B (Table 1) as a fraction more polar then compounds **1** and **2** [*n*-hexane−ethyl acetate (9:1) as the eluent] to obtain 0.056 g (yield 14%) of **3** as a

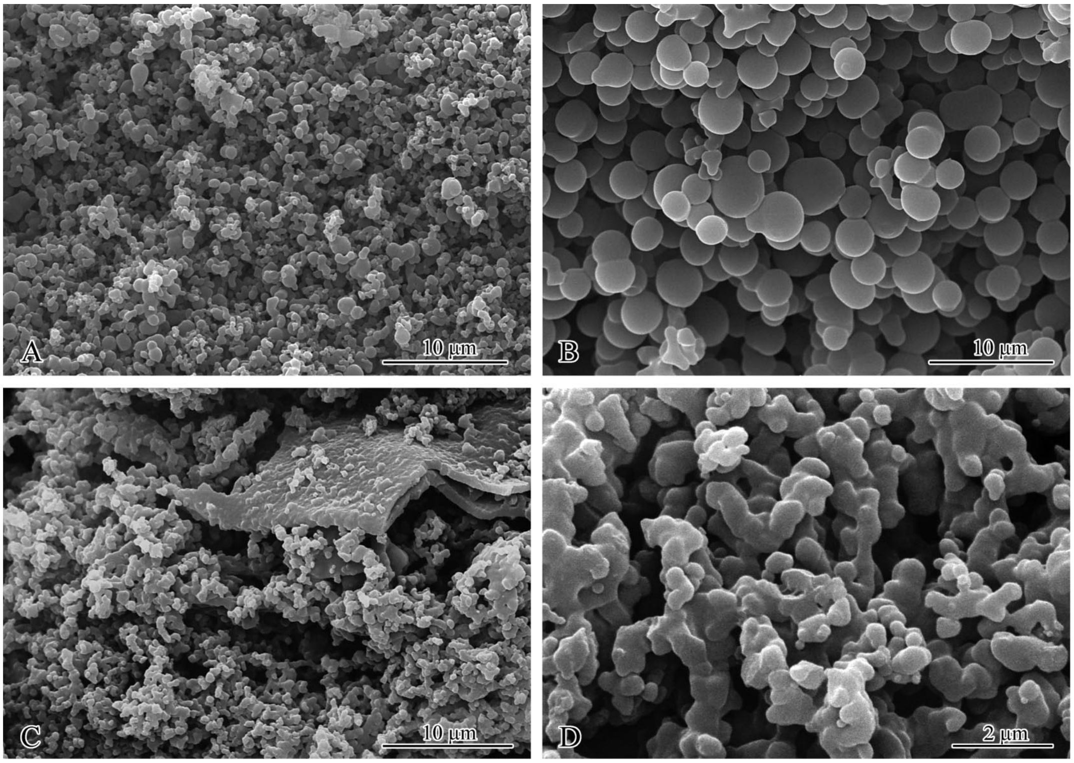


Figure 9. Molecular aggregate structure found by SEM analysis of poly-**BF1** precipitated from a dichloromethane solution with ethanol. Top left: nanoparticles obtained with poly-**BF1-AP**; top right: microspheres obtained with poly-**BF1-AP**; bottom: large aggregates obtained with poly-**BF1-SP** shown at different magnification ratios.

colorless oil, which crystallized on standing (mp 125–126.5 °C). ^{1}H NMR (200 MHz, CDCl$_3$): 2.20 (s, 3H), 3.03 (dd, *J* = 13.6, 8.7, 1H), 3.51 (dd, *J* = 13.5, 4.2, 1H), 4.54 (dd, *J* = 8.5, 4.1, 1H), 6.90 (d, *J* = 7.9, 2H), 6.97–7.43 (m, 16H). MS (ESI): *m*/*z* 423 [M + 23]$^+$.

Dimer 4. The mixture of dimers **4** and **5** was isolated as a fraction more polar than compounds **6** and **7** [*n*-hexane−ethyl acetate (9:1) as the eluent] from the above-mentioned flash chromatography purification of the *n*-hexane-soluble fraction of entry B (Table 1). Isomer **4** was purified by semipreparative HPLC by using the following conditions: VWR, LaPrep, P130 HPLC pump and P311 spectrophotometer (scanning absorbance) online detector; Chromolith Semiprep RP-18 end-capped 100–10 mm HPLC column (10 mm D × 10 cm L); 3.0 mL/min of flow rate at room temperature; constant mobile phase: 10% water, 45% acetonitrile, 45% methanol (v/v); retention time 8.9 min. Dimer **4** was isolated as white sticky solid (0.11 g, yield 17%). ^{1}H NMR (200 MHz, CDCl$_3$): 0.86 (t, *J* = 7.3, 3H), 1.00 (t, *J* = 6.6, 3H), 2.23 (s, 3H), 2.31 (s, 3H), 3.24 (d, *J* = 12.4, 1H), 3.57 (dd, *J* = 14.5, 5.2, 1H), 3.71–4.07 (m, 7H), 6.07 (d, *J* = 7.9, 2H), 6.36 (d, *J* = 7.4, 2H), 6.67 (m, 3H), 6.76–6.95 (m, 5H), 7.02 (m, 3H), 7.16 (m, 3H), 7.28 (m, 1H), 7.39 (m, 1H), 7.49 (d, *J* = 7.4, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): 13.6 (C-A-*bf1*), 13.9 (C-A-*bf2*), 21.3 (C-1″-*bf1*), 21.4 (C1″-*bf2*), 35.3 (C-D-*bf2*), 46.7 (C-D-*bf1*), 49.3 (C-1-*bf2*), 58.4 (C-1-*bf1*), 59.3 (C−B-*bf1*), 59.8 (C−B-*bf2*), 122.7 (C-4-*bf2*), 123.1 (C-4-*bf1*), 123.4 (C-7-*bf1*), 124.3 (C-7-*bf2*), 125.9 (C-4‴), 126.7 (C-5-*bf2*, C-6-*bf2*), 126.9 (C-3‴/5‴), 127.1 (C-5-*bf1*), 127.5 (C-6-*bf1*), 127.7 (C-3′/5′-*bf1*), 127.9 (C-3′/5′-*bf2*), 128.2 (C-2′/6′-*bf1*), 129.3 (C-2′/6′-*bf2*), 129.5 (C-2‴/6‴), 131.5 (C-1′-*bf2*), 132.3 (C-1′-*bf1*), 134.2 (C-2-*bf2*), 134.6 (C-2-*bf1*), 136.4 (C-1‴), 136.5 (C-4′-*bf1*), 137.2 (C-4′-*bf2*), 144.2 (C-3a-*bf2*), 144.3 (C-3a-*bf1*), 147.3 (C-7a-*bf2*), 150.5 (C-7a-*bf1*), 152.1 (C-3-*bf2*), 154.0 (C-3-*bf1*), 164.7 (C-*C*-*bf2*), 164.8 (C-*C*-*bf1*). MS (ESI): *m*/*z* 681 [M + 23] $^+$.

Dimer 5. The mixture of dimers **4** and **5** was isolated from the above-mentioned flash chromatography purification of the *n*-hexane-soluble fraction of entry B (Table 1) as a fraction more polar than compounds **6** and **7** [*n*-hexane−ethyl acetate (9:1) as the eluent]. Isomer **5** was purified by semipreparative HPLC in the following conditions: VWR, LaPrep, P130 HPLC pump and P311 spectrophotometer (scanning absorbance) online detector; Chromolith Semiprep RP-18 end-capped 100–10 mm HPLC column (10 mm D × 10 cm L); 3.0 mL/min of flow rate at room temperature; constant mobile phase: 10% water, 45% acetonitrile, 45% methanol (v/v); retention time 11.4 min. Dimer **5** was isolated as white sticky solid (0.033 g, yield 5%). ^{1}H NMR (200 MHz, CDCl$_3$): 0.91 (t, *J* = 6.9, 3H), 1.04 (t, *J* = 7.3, 3H), 2.32 (s, 3H), 2.37 (s, 3H), 3.22 (m, 2H), 3.44 (dd, *J* = 14.3, 6.7, 1H), 3.71–4.21 (m, 6H), 6.42 (d, *J* = 7.2, 2H), 6.51 (d, *J* = 7.6, 2H), 6.64 (d, *J* = 7.3, 1H), 6.80–7.19 (m, 15H), 7.43 (d, *J* = 7.4, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): 13.8 (C-A-*bf1*), 14.0 (C-A-*bf2*), 21.5 (C-1″-*bf1*, C-1″-*bf2*), 36.1 (C-D-*bf2*), 47.0 (C-D-*bf1*), 48.6 (C-1-*bf2*), 58.7 (C-1-*bf1*), 59.5 (C−B-*bf1*), 61.0 (C−B-*bf2*), 122.5 (C-4-*bf2*), 122.8 (C-4-*bf1*), 123.9 (C-7-*bf1*), 124.8 (C-7-*bf2*), 126.1 (C-4‴), 126.2 (C-6-*bf2*), 126.7 (C-5-*bf2*), 126.8 (C-5-*bf1*), 126.9 (C-3‴/5‴), 127.3 (C-6-*bf1*), 128.1 (C-3′/5′-*bf1*), 128.3 (C-3′/5′-*bf2*, C-2′/6′-*bf1*), 129.0 (C-2′/6′-*bf2*), 129.5 (C-2‴/6‴), 131.9 (C-1′-*bf2*), 132.5 (C-1′-*bf1*), 135.0 (C-2-*bf1*, C-2-*bf2*), 136.7 (C-1‴), 136.9 (C-4′-*bf2*), 137.3 (C-4′-*bf1*), 144.0 (C-3a-*bf2*), 144.3 (C-3a-*bf1*), 147.6 (C-7a-*bf2*), 150.0 (C-7a-*bf1*), 152.3 (C-3-*bf2*), 154.6 (C-3-*bf1*), 164.9 (C-*C*-*bf1*), 165.1 (C-*C*-*bf2*). MS (ESI): *m*/*z* 681 [M + 23] $^+$.

Dimer 6. Isomer **6** was isolated by flash chromatography [*n*-hexane−ethyl acetate (9:1) as the eluent] from the *n*-hexane-soluble fraction of entry B (Table 1) as a fraction more polar than compound **3** to obtain 0.040 g of a colorless oil (yield 6%). ^{1}H NMR (200 MHz, CDCl$_3$): 1.08 (m, 6H), 2.24 (s, 3H), 2.32 (s, 3H), 3.52 (d, *J* = 12.6, 1H), 3.93–4.24 (m, 6H), 4.42 (d, *J* = 12.9, 1H), 4.70 (s, 1H), 6.43 (d, *J* = 7.9, 2H), 6.51 (d, *J* = 7.8, 2H), 6.64 (d, *J* = 7.5, 2H), 6.76 (d, *J* = 7.2, 1H), 6.85–7.21 (m, 12H), 7.41 (m, 1H), 7.70 (d, *J* = 7.4, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): 14.1 (C-A-*bf1*, C-A-*bf2*), 21.2 (C-1″-*bf2*), 21.4 (C-1″-*bf1*), 32.3 (C-D-*bf2*), 44.4 (C-D-*bf1*), 56.0 (C-3-*bf2*), 59.9 (C−B-*bf1*, C−B-*bf2*), 60.2 (C-1-*bf1*), 122.9 (C-4-*bf1*), 123.0 (C-7-*bf2*), 123.9 (C-4-*bf2*), 124.6 (C-7-*bf1*), 126.1 (C-4‴), 126.5 (C-6-*bf2*), 127.1 (C-3‴/5‴), 127.2 (C-5-*bf1*), 127.8 (C-6-*bf1*, C-2′/6′-*bf2*), 127.9 (C-2′/6′-*bf1*), 128.0 (C-5-*bf2*), 128.3 (C-3′/5′-*bf1*), 129.1 (C-3′/5′-*bf2*), 129.4 (C-2‴/6‴),132.4 (C-1′-*bf1*), 135.8 (C-4′-*bf2*), 136.0 (C-2-*bf1*), 136.3 (C-1′-*bf2*), 137.1 (C-4′-*bf1*, C-1‴), 137.4 (C-2-*bf2*), 143.7 (C-7a-*bf2*), 143.9 (C-3a-*bf1*), 149.1 (C-3a-*bf2*), 150.0 (C-7a-*bf1*), 152.4 (C-1-*bf2*), 155.0 (C-3-*bf1*), 165.5 (C-*C*-*bf2*), 165.7 (C-*C*-*bf1*). MS (ESI): *m*/*z* 681 [M + 23] $^+$.

Dimer 7. Isomer **7** was isolated by flash chromatography [*n*-hexane−ethyl acetate (9:1) as the eluent] from the *n*-hexane-soluble fraction of entry B (Table 1) as a fraction more polar than compound **6** to obtain 0.016 g of a colorless oil (yield 2%). ^{1}H NMR (200 MHz, CDCl$_3$): 1.02 (m, 6H), 2.24 (s, 3H), 2.29 (s, 3H), 3.53 (d, $J = 12.8$, 1H), 3.83–4.17 (m, 6H), 4.37 (d, $J = 12.9$, 1H), 4.46 (s, 1H), 6.35 (d, $J = 7.8$, 2H), 6.67 (m, 3H), 6.76 (d, $J = 7.9$, 2H), 6.83–7.20 (m, 12H), 7.41 (m, 1H), 7.49 (d, $J = 7.3$, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): 14.0 (C-A-*bf1*, C-A-*bf2*), 21.2 (C-1″-*bf2*), 21.4 (C-1″-*bf1*), 32.6 (C-D-*bf2*), 43.4 (C-D-*bf1*), 56.1 (C-3-*bf2*), 59.8 (C−B-*bf1*, C−B-*bf2*), 60.3 (C-1-*bf1*), 122.4 (C-7-*bf2*), 122.8 (C-4-*bf1*), 124.1 (C-4-*bf2*), 124.5 (C-7-*bf1*), 126.1 (C-4‴), 126.5 (C-6-*bf2*), 127.1 (C-5-*bf1*, C-6-*bf1*, C-3‴/5‴), 127.8 (C-5-*bf2*), 128.0 (C-2′/6′-*bf1*, C-2′/6′-*bf2*), 128.2 (C-3′/5′-*bf1*), 129.1 (C-3′/5′-*bf2*), 129.5 (C-2‴/6‴), 132.3 (C-1′-*bf1*), 135.8 (C-2-*bf1*), 136.1 (C-4′-*bf2*), 136.7 (C-1′-*bf2*), 137.0 (C-4′-*bf1*), 137.3 (C-1‴), 138.5 (C-2-*bf2*), 143.9 (C-3a-*bf1*), 144.4 (C-7a-*bf2*), 148.5 (C-3a-*bf2*), 149.7 (C-7a-*bf1*), 150.3 (C-1-*bf2*), 154.8 (C-3-*bf1*), 165.9 (C-*C bf1*/C-*C bf2*). MS (ESI): *m*/*z* 681 [M + 23] $^+$.

Poly[ethyl 1-methylene-3-(4-methylphenyl)-1*H*-indene-2-carboxylate] (Poly-BF1-AP). The *n*-hexane-insoluble fraction was used in the characterization (NMR, thermoreversibility analysis, mass spectrometry analysis, DSC, MWD characterization, and absorption and emission spectra) in most cases without further purification. For the SEM studies, the *n*-hexane-insoluble fraction of entry J was dissolved into dichloromethane and precipitated in the excess of a bad solvent (ethanol) to give a white solid. ^{1}H NMR (200 MHz, CDCl$_3$): see Figure 2. ^{13}C NMR (150 MHz, CDCl$_3$): 13.6 (CH$_3$, C-*A*), 21.3 (CH$_3$, C-1″), 48.5 (CH$_2$, C-*D*), 57.5 (quat, C-1), 59.0 (CH$_2$, C-*B*), 122.5 (CH, C-4), 124.5 (CH, C-7), 126.3 (CH, C-2′/6′, C-3′/5′, C-5, C-6), 128.3 (CH, C-3′/5′), 129.9 (CH, C-2′/6′), 131.3 (quat, C-1′), 134.3 (quat, C-2), 135.9 (quat, C-4′), 142.6 (quat, C-3a), 148.6 (quat, C-7a), 151.5 (quat, C-3), 163.8 (C═O, C−*C*).

SEC-MALS. The MWD characterization of poly-**BF1** samples was performed by a MALS light scattering photometer online to a SEC chromatographic system. The SEC-MALS system and the corresponding experimental conditions were identical to those used in our previous study[15,16,18] and will not be reported in detail here.

NMR Spectroscopy. NMR experiments were performed with a Bruker DRX-600 AVANCE spectrometer, equipped with a *xyz* gradient unit, operating at 600.13 and 150.89 MHz for ^{1}H and ^{13}C, respectively. NOESY[19] and dqf-COSY[20] spectra for **4**, **5**, **6**, and **7** were acquired with 2048 complex points for 256 experiments with 6 s recycle and TPPI phase cycle.[21] A 90° shifted squared-sine window function was used in both dimensions for every set of data and zero-filling to 1024 points was applied along F1. For NOESY spectra, mixing time of 200, 400, and 800 ms were used. NMR data were processed by using the NMRpipe[22] software (version 3.3), and 2D spectra were analyzed with the SPARKY[23] software. Gradient-selected ^{1}H−^{13}C HSQC[24] and HMBC[25] spectra were acquired with 2048 complex points for 256 experiments with 2 s recycle. $^1J_{\mathrm{CH}}$ and $^nJ_{\mathrm{CH}}$ were fixed at 145 and 10 Hz, respectively. For HMBC a low-pass *J*-filtering was applied.

Mass Spectrometry. In HPLC-MS experiments, an Agilent 1100 LC/MSD (column: Agilent Zorbax 5 μm Eclipse XDB-C$_8$, 4.6 × 150 mm; UV detection) was used. In MALDI-TOF experiments, the polymer was dissolved into chloroform at a concentration of 5×10^{-5} mol/L. DTH (2,6,7-trihydroxyanthracene, dithranol) (Fluka) was used as a matrix. It was dissolved into dichloromethane in a concentration range of 0.1–0.2 M. Mixing equal volumes from the matrix and polymer solutions gave the resultant polymer/matrix solution which was used to spot the MALDI sample plate. A Bruker Ultraflex TOF/TOF instrument (Bruker Daltonics, Inc., Billarica, MA) with conventional nitrogen laser (337 nm) was used in linear mode.

Mass spectra of the volatile compounds were obtained by a Saturn 2000 ion trap coupled with a Varian 3800 gas chromatograph (Varian, Walnut Creek, CA) and using a DB-5 column (30 m, 0.25 mm i.d., 0.25 μm film thickness, Supelco). The electron ionization (70 eV) mode was used with a source temperature of 220 °C. A ThermoFinnigan LCQ-Deca ion trap mass spectrometer operating with a electrospray source was also used. The positive mode, with the spray voltage at 4.5 kV, the capillary temperature 220 °C, and the capillary voltage 15 V, was used.

Differential Scanning Calorimetry. Differential scanning calorimetric (DSC) analysis was performed with a Perkin-Elmer DSC-7 instrument and PYRIS software (version-5). Temperature axis and cell constant were calibrated with indium. Weighed samples of poly-**BF1-AP** in pinholed aluminum pans were heated at 20 °C/min over a temperature range of 40–340 °C under nitrogen purge (20 mL/min).

Scanning Electron Microscopy (SEM) Studies. The material was mounted on aluminum holders by carbon conductive glue and coated with 20 nm gold in a Balzer's MED 010 sputtering device. The samples were observed with a Philips XL20 scanning electron microscope operating at an accelerating voltage of 20 kV.

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Supporting Information Available: HSQC and HMBC spectra of **poly BF1-AP**; structures of two models of dimer **4** compatible with the NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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