

Polymer Communication

[60]Fullerene-initiated bulk polymerization of *N*-vinylcarbazole under the microwave irradiation

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Abstract

The [60]fullerene-initiated “charge-transfer” bulk polymerization reaction of *N*-vinylcarbazole (NVC) under microwave irradiation (490 W) has been demonstrated. In comparison with the C₆₀-initiated polymerization reaction of NVC in the water bath at 70°C, carrying out the polymerization reaction in the microwave oven was found to be advantageous due to the remarkable decrease in the time necessary to carry out reaction, and to the considerable improvement in yield of poly(*N*-vinylcarbazole). A reasonable polymerization reaction pathway via C₆₀–NVC ion–radical pairs is suggested. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Bulk polymerization; Microwave irradiation; [60]Fullerene

1. Introduction

The systematic development of synthetic methodologies for the functionalization of fullerenes has paved the way for the preparation of novel organic and polymeric fullerene derivatives of interest in the search of new materials with marvelous photophysical, electric and magnetic properties as well as biological activities [1–4]. As a new form of carbon, [60]fullerene can be covalently incorporated into a variety of polymers by copolymerization or grafting [5,6]. This covalent attachment of C₆₀ to specific polymers may allow combination of the splendid characteristics of fullerene with the outstanding properties of the polymeric matrix to generate new fullerene-based specialty polymeric materials. Over the past several years, there are already a large number of articles concerning the polymeric modification of [60]fullerene [2]. However, to our knowledge, little attention has been paid to the polymerization of electron-rich vinyl-monomers initiated directly by [60]fullerene.

As observed in many experiments, [60]fullerene is a redox-active chromophore, which can reversibly accept up to six electrons in electrochemical reductions or in chemical conversions to form fulleride anions, and prefers to react with electron-rich reagents [7]. These observations show

the possibility wherein C₆₀ can be used directly to initiate polymerization reactions of electron-rich vinyl-monomers. This idea was confirmed by our recent experimental results. Although C₆₀ and its polyanions salts [C₆₀ⁿ⁻(M⁺)_n, M = Li, Na, K] cannot be used to initiate the anionic polymerization of vinyl-monomers [5,8], C₆₀ may initiate “charge-transfer” bulk polymerization of electron-rich organic monomers under microwave irradiation and conventional water-bath heating conditions. Here we first used [60]fullerene as initiator in the bulk under the microwave irradiation to synthesize poly(*N*-vinylcarbazole) (yield >70%), which is one of a number of vinyl polymers with aromatic pendant groups that have elicited considerable interest as potential commercial photoconductor systems and exhibit interesting electrical properties [9].

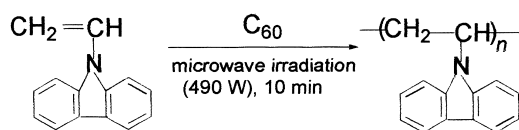
2. Experimental

2.1. Reagents and instrumentation

2.1.1. Reagents

Tetrahydrofuran (THF) was dried, deoxygenated and distilled before use. Unless noted otherwise, other analytically pure reagents, for example, methanol, hydrochloric acid, etc. were used as received.

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2.1.2. Instrumentation

Near-infrared (NIR) absorption spectra in THF were measured on a Shimadzu UV-365 UV–VIS–NIR recording spectrophotometer. Ultraviolet–visible (UV–VIS) absorption spectra in THF were recorded on an UV-240 spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet FT-IR-5DX spectrophotometer using KBr pellets. ^{13}C NMR spectra in CDCl_3 were run on a Bruker MSL-600 NMR spectrometer. X-ray diffraction spectra were measured on a Japanese Science D/Max-RB diffractometer (Cu target). Thermal properties of the samples were measured using a Dupont 2000 thermogravimetric analyzer (TGA). The molecular weight of the polymer was analyzed by Waters 410 gel permeation chromatograph (GPC) in tetrahydrofuran solutions with linear polystyrene standards. This GPC system was equipped with a refractive index detector (External RI), a viscosity detector (Viscotek Model T60) and a light scattering (LS) detector (Viscotek Model T60). Electron spin resonance spectra were recorded on a Bruker ER200D-SRC spectrometer, and g -values were determined by calibration with DPPH (α, α' -diphenyl- β -picryl hydrazyl).

2.2. Synthesis of poly(*N*-vinylcarbazole)

C_{60} (purity >99.99%) was obtained from the Fullerene Institute of Wuhan University of China. *N*-vinylcarbazole [Fluka, Purity (GC) $\geq 98\%$, m.p. 65°C] was recrystallized twice from methanol at 40°C , freeze-dried, and stored in vacuum in the dark before use. Microwave polymerization reactions were carried out in sealed argon-filled thick-walled Pyrex tubes placed in the microwave oven (LG Electronics Tianjin Appliances Co. Ltd., China; microwave frequency: 2450 MHz; output power: 490 W). After a deoxygenated mixture of C_{60} (0.02 g, 0.028 mmol) and NVC (0.19, 0.38, 0.76, 0.86, 1.07, 1.61, and 3.22 g, respectively) was heated for 10 min, the melted reaction mixture was allowed to cool to room temperature. This mixture was dissolved in the dried and deoxygenated THF under purified argon atmosphere, and then filtered to remove any unreacted C_{60} . Unexpectedly, only a mere trace of C_{60} residues was observed on the filter paper, this implying that most of C_{60} in THF solution might be fulleride anions. A transparent reddish brown filtrate obtained was divided into two equal parts. One was analyzed directly by near-infrared (NIR) spectroscopy and UV–VIS absorption spectroscopy. Another part of the filtrate was poured into the acidified methanol solution to give a gray polymer. This crude product was redissolved in THF under vigorous stirring,

filtered to remove C_{60} residues, and reprecipitated with acidified methanol to give a white solid (this procedure was repeated at least three times). Solvent residues were removed by freeze drying under vacuum for several hours. The structure of this polymer was confirmed by UV–VIS, ^{13}C NMR, FTIR, TGA and XRD techniques, and is in very good agreement with that of the standard PVK [10]. The synthetic routine is shown in Scheme 1. In contrast, after the pure NVC monomer was heated for 10 min in a microwave oven in the absence of C_{60} , no polymer was obtained.

3. Results and discussion

As described in Section 2, the reddish brown transparent filtrate obtained was divided into two equal parts. One was poured into the acidified methanol solution to give a gray crude product. Another part of filtrate was analyzed directly by near-infrared (NIR) spectroscopy and UV–VIS absorption spectroscopy. It is found that a characteristic absorption at 1090 nm assignable to C_{60} radical anion was detected in the NIR spectrum, suggesting that [60]fullerene moieties in the above THF solution should be fulleride anions (C_{60} itself is not soluble in THF). Further, the UV–VIS absorption spectrum of the filtrate is also apparently different from that of pure PVK. The latter is essentially transparent at wavelengths longer than 380 nm, whereas the former has apparent absorption bands in the longer wavelength, in which two weak new peaks at 404 and 432 nm were detected. Similarly, Sension et al. [11] and Kamat [12] also observed that C_{60} radical anion has weak absorbance at approximately 420 nm. These findings demonstrated clearly that [60]fullerene moieties in the filtrate were C_{60} radical anions, which were formed by the electron transfer between the electron donor (NVC) and the acceptor (C_{60}). ESR results also confirmed the “charge-transfer” phenomenon between C_{60} and NVC. At ambient temperature, no ESR signals for either NVC or C_{60} were detected, whereas ESR spectra of the simple blends of C_{60} and NVC (i.e. C_{60} -doped NVC) show a small ESR signal whose g -value and linewidth (ΔH_{pp}) are 2.0026, 1.8 G, respectively, this implying that there is a weak charge transfer between C_{60} and NVC in the mixture. Obviously, one may imagine that the charge transfer from NVC monomer to [60]fullerene would become easier under the microwave irradiation.

In comparison with the C_{60} -initiated polymerization reaction of NVC in the water bath at 70°C [slightly higher than its melting point (65°C)], carrying out the polymerization reaction in the microwave oven was found to be advantageous due to the remarkable decrease in the time necessary to carry out reaction, and to the considerable improvement in yield of poly(*N*-vinylcarbazole) (70% yield as opposed to a 8% yield after 10 min of conventional heating) under the same C_{60} /NVC molar ratio and reaction time as that of the former one, which may be due to the high temperatures achieved very rapidly on microwave irradiation.

Table 1
Polymerization conditions and related experimental data

Samples	CY ₁	CY ₂	CY ₃	CY ₄	CY ₅	CY ₆	CY ₇
Feed molar ratio (NVC/C ₆₀)	35	70	140	160	200	300	600
Reaction time (min)	10	10	10	10	10	10	10
Yield (%) ^a	70	71	75	75	73	70	72
Molecular weight ($\times 10^{-4}$)							
M_n	6.22	3.26	3.33	6.69	0.72	0.71	0.68
M_w	13.57	8.70	8.72	15.58	4.69	4.06	2.68
Pd	2.18	2.67	2.62	2.32	6.51	5.72	3.94
Radius of gyration (nm)							
R_{gw}	9.26	6.44	7.13	7.20	4.22	4.04	3.19
R_{gn}	7.11	4.13	5.20	5.50	2.23	2.34	1.99

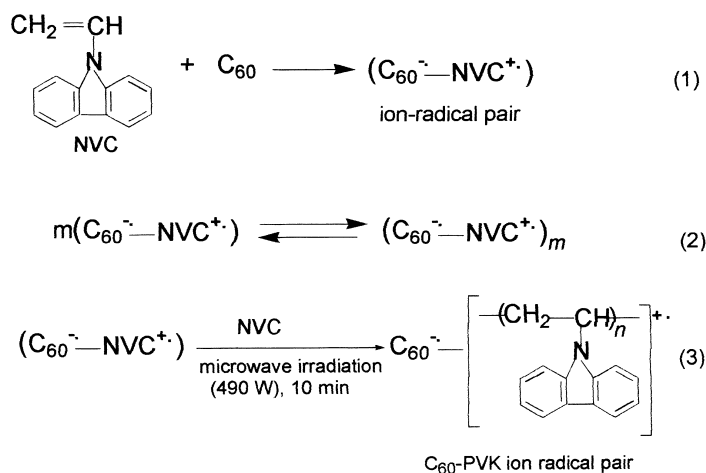
^a Based on the weight of NVC monomer.

However, the GPC/RI/DV/LS experiments showed clearly that the different heating methods (microwave and water-bath heating) have no striking effect on the molecular masses and polydispersity of the resultant polymer in the same initiator concentration. Interestingly, the GPC/LS chromatogram of the product prepared in the microwave oven shows two peaks: a big peak corresponding to the PVK polymer and a small peak. Because the M_{peak} of the small peak is very close to the molecular mass of a NVC dimer, this peak may be assigned to the dimer of *N*-vinylcarbazole. Table 1 gives the microwave polymerization reaction conditions and the related experimental data.

As the C₆₀/NVC molar ratio changed from (1:160 to 1:200) to (1:300 to 1:600), the molecular weight decreases apparently. Among these four samples, weight-average and number-average molecular weights of the polymer CY₄ are considerably higher than that of the other three samples (CY₅, CY₆ and CY₇), whereas the molar masses of the last three samples are similar. If we assume that all C₆₀ molecules were completely used to initiate “charge-transfer” polymerization of the NVC monomer, similar to the initiation mode of anionic polymerization of some

vinyl-monomers exhibited by *n*-butyllithium, the higher the initiator concentration, the smaller the molecular weight of the resultant polymer. However, the observed results are not so. A possible interpretation is that, in the bulk polymerization process of monomer, the reversible association equilibrium between the (C₆₀⁻-NVC⁺) charge-transfer (CT) complexes, as shown in Scheme 2, cannot be negligible. Only individual (C₆₀⁻-NVC⁺) CT complex can further initiate the polymerization of electron-rich NVC monomer to produce polymeric CT complex (C₆₀⁻-PVK⁺). Obviously, the higher the initiator (C₆₀) concentration, the bigger the association degree of (C₆₀⁻-NVC⁺), and consequently, the smaller the concentration of the free (C₆₀⁻-NVC⁺) complex. The actual reaction may be more complicated and requires further investigations.

In summary, we used [60]fullerene as an initiator to initiate the bulk polymerization of electron-rich *N*-vinylcarbazole monomer under microwave irradiation. The yield of the resultant polymer is higher than 70%. Further studies on the reaction mechanisms based on a more detailed analysis of polymer architectures and kinetics are currently in progress.



Scheme 2.

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