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New Route to Incorporation of [60]Fullerene into Polymers via the Benzocyclobutenone Group

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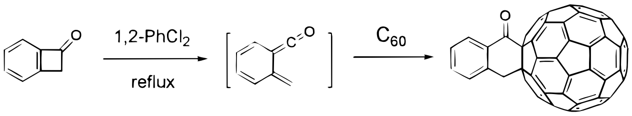
Since the development of methods for mass production of [60]fullerene (C_{60}),[1] the rich chemistry of C_{60} has opened an avenue to new materials research and applications.[2] Incorporation of C_{60} into a polymer has been recognized as a simple means of combining the unique properties of C_{60} with macromolecular characteristics such as mechanical strength and good processability.[2,3] [60]Fullerene itself can be directly incorporated into a variety of polymers by copolymerization or grafting.[4] Chemically functionalized C_{60} derivatives are either introduced into a condensation polymer through copolymerization or attached onto a polymer by grafting.[4,5] In the former case, the actual amount of C_{60} incorporated in the polymer is usually much less than that in feed, which necessitates accurate determination of the C_{60} content in the polymer in order to establish the structure−property relationship. However, there is no general method available for all types of C_{60} polymers. All the known methods are only suitable for quantification of specific types of C_{60} polymers, such as thermogravimetry (TG),[4d] UV−vis spectroscopy,[4b] and gel permeation chromatography (GPC),[4a] or give an estimated value of the C_{60} content (e.g., from the mass ratio of a reacted monomer and C_{60}[6]). If quantitative incorporation of C_{60} into a polymer can be achieved through a specific reaction, quantification of C_{60} in the resulting C_{60} polymer may not be needed. For example, a series of copolyamides containing a controlled amount of C_{60} in the main chain were obtained by polycondensation of [60]fullerenebisacetic acid, isophthalic acid, and 4,4′-oxydianiline.[7] Similarly, if the functional group present in a polymer is able to react with C_{60} specifically and quantitatively, the polymer containing a known amount of C_{60} on the side chain can be obtained. The reaction of an azide with C_{60} has been utilized for this purpose.[8] The weight percent of C_{60} incorporated was found to be slightly less (ca. 80%) than the theoretical value (i.e., the azide content). Clearly, a functional group that undergoes a high-yield, specific monoaddition reaction with C_{60} is desirable.

Benzocyclobutenone (BCBO) is such a compound that upon thermal activation generates a reactive diene, α-oxo-*o*-quinodimethane,[9] which subsequently undergoes a [4 + 2] cycloaddition reaction with C_{60} (Scheme 1).[10] Thermolysis of BCBO in refluxing 1,2-dichlorobenzene in the presence of equimolar C_{60} afforded cleanly the corresponding BCBO−C_{60} adduct, along with unreacted BCBO. It is conceivable that the use of an excess of C_{60} should lead eventually to quantitative conversion of BCBO. Accordingly, BCBO can be used as a handle to link C_{60} with a polymer and, more importantly, the amount of BCBO present in the precursor polymer should be identical with the C_{60} content in the resulting polymer. In this paper, a new route to incorporation of C_{60} into vinyl polymers (e.g., polystyrene and polyethylene) is demonstrated based on the unique BCBO−C_{60} cycloadditon chemistry.

Scheme 1. [4 + 2] Cycloaddition of Benzocyclobutenone and C_{60}



Benzocyclobutenone can be easily prepared in large quantities from anthranilic acid, homophthalic anhydride, or *o*-toluoyl chloride according to known methods.[11] A simple nitration followed by reduction (e.g., Fe or $SnCl_2$) gave a key functionalized BCBO, 5-aminobenzocyclobutenone, which was used to prepare a BCBO-containing vinyl monomer (**1**; Figure 1). Using monomer **1**, BCBO can thus be incorporated into a wide spectrum of vinyl polymers as a pendant group through copolymerization with vinyl monomers (e.g., styrene).

Thus, free-radical polymerization of monomer **1** and styrene in different feed ratios afforded the copolymers BCBO−PSt **2a**−**c** (Figure 1). The presence of the BCBO group in the polymer was evidently shown by IR with a carbonyl stretch at 1765 cm^{-1} characteristic of BCBO. The BCBO content in polymers **2a**−**c** depends on the feed ratio of monomer **1** and styrene and can be quantified from the linear calibration curve of the BCBO absorbance versus its mole concentration in polystyrene, established by a UV spectroscopic method. The incorporation of monomer **1** into the polymers was effective and quantitative, as indicated by comparison of the feed ratio with the measured one. For the syntheses of BCBO−PSt **2a**−**c**, the molar percent of **1** in feed was 5, 10, and 15%, respectively. By UV analysis the molar percent of BCBO was found to be 3.94, 9.77, and 12.6% for BCBO−PSt **2a**−**c**, respectively (Table 1).

The C_{60}-containing polymers, C_{60}−PSt **3a**−**c**, were readily obtained from the reaction of BCBO−PSt **2a**−**c** and C_{60} in refluxing 1,2-dichlorobenzene (Figure 1).[12] Incorporation of C_{60} in the polymer was confirmed by a number of spectroscopic means. The FTIR spectra of all C_{60}−PSt showed the disappearance of a peak at 1765 cm^{-1} due to the BCBO's ketone group (e.g., **3a** and **5** in Figure 2). The expected new carbonyl peak attributed to the ketone group of the BCBO−C_{60} adduct at 1688 cm^{-1} as reported for the model adduct[10] (Scheme 1) was overlapped with the amide peak from monomer **1**. The rest is essentially the same as that of the parent BCBO−PSt, except for an additional weak peak at 528 cm^{-1} due to the functionalized C_{60} cage in the polymer. Moreover, the peak intensity at 528 cm^{-1} increased gradually with an increase of the C_{60} content in the polymer (from **3a** to **3b**). Similar to other C_{60}-grafted polystyrenes,[8] all C_{60}−PSt **3** had a broad set of resonances between 141 and 148 ppm in their ^{13}C NMR spectra. The characteristic resonance at 145 ppm for free C_{60} was absent in all spectra. The ^{1}H NMR spectra of C_{60}−PSt **3a**−**c** showed a singlet at 4.80 ppm assigned to the two benzylic protons on the BCBO moiety, which

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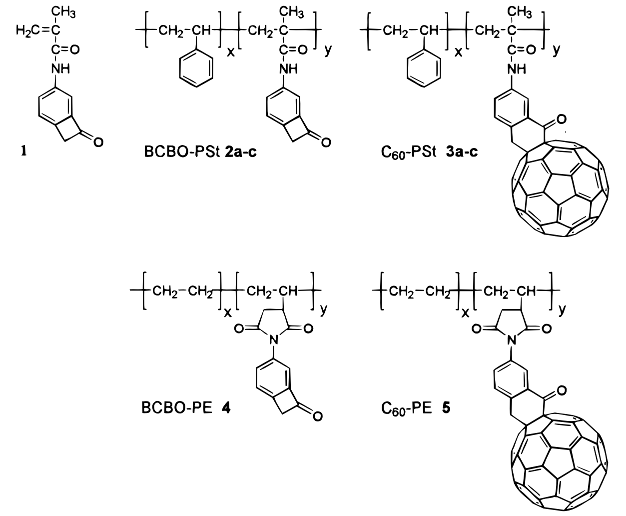

Figure 1. BCBO monomer and BCBO- and C_{60}-containing vinyl polymers.

Table 1. Characterization of BCBO- and C_{60}-Containing Polystyrenes

	BCBO in **2**		C_{60} in **3**					
polymer	wt %[a]	mol %[b]	wt %[c]	mol %[b]	$M_w \times 10^{-4}$	PDI	T_d[d] (°C)	T_g[e] (°C)
2a	7.35	3.94			3.97	2.2	376	97
2b	17.3	9.77			3.98	2.1	372	112
2c	21.8	12.6			1.60	1.8	371	128
3a			22.5	4.18	4.27	2.2	382	124
3b			39.4	9.33	4.16	2.5	379	156
3c			43.8	11.2	1.75	2.0	380	[f]

[a] Determined by UV analysis at 320 nm. [b] Calculated from molecular weights of repeat units. [c] Determined by UV analysis at 330 nm. [d] Onset temperature for 5% weight loss, as assessed by TG at a heating rate of 10 °C/min under nitrogen. [e] Measured by DSC at a heating rate of 10 °C/min under nitrogen. [f] Transition was too broad to determine a T_g.

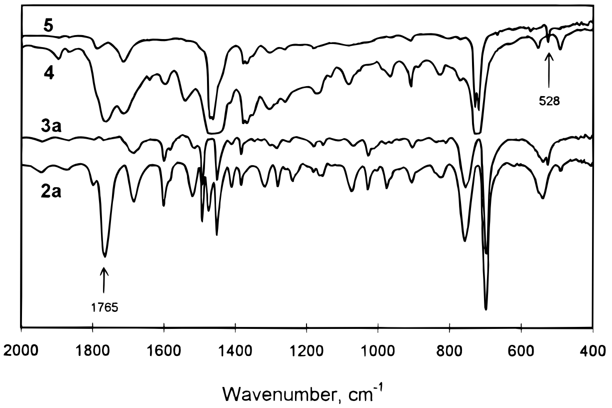

Figure 2. IR spectra (400−2000 cm^{-1}) of BCBO−PSt **2a**, C_{60}−PSt **3a**, BCBO−PE **4** and C_{60}−PE **5**.

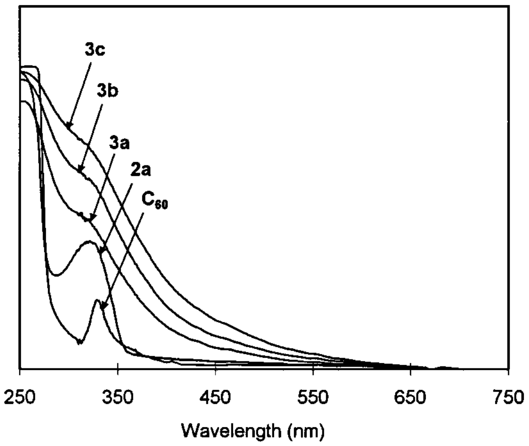

Figure 3. UV−vis spectra of pure C_{60} (1.5×10^{-3} mg/mL), BCBO−PSt **2a** (0.2 mg/mL), and C_{60}−PSt **3a**−**c** (1.6×10^{-2} mg/mL) in dichloromethane.

is clearly different from the corresponding protons at 4.0 ppm for BCBO−PSt **2a**−**c**. Finally, the presence of C_{60} in the polymer chain is evident by its characteristic absorbance. The UV−vis spectrum of BCBO−PSt (e.g., **2a**) displayed a peak with λ_{max} near 320 nm (Figure 3). However, C_{60}−PSt (e.g., **3a**) had a broad absorption with tailing up to 650 nm, which is beyond the absorption edge of C_{60}. Furthermore, as the amount of C_{60} increases from **3a** to **3c**, the intensity also increases proportionally (Figure 3). It is known that C_{60} derivatives show weaker or no characteristic absorption (λ_{max} 330 nm) of pure C_{60}, depending on the degree of substitution.[4e] Thus, the C_{60} moiety in polymers **3** should have a π-conjugation extended to the attached benzoyl group.

GPC analysis indicated that the weight-average molecular weights of C_{60}−PSt **3** were slightly higher than those of parent BCBO−PSt **2** (Table 1). Moreover, GPC traces of both BCBO and C_{60} polymers were monomodal with nearly equal polydispersity indices (PDI). Therefore, a specific 1:1 addition occurred for all the BCBO groups in the precursor polymers **2**; otherwise, multiple addition would lead to the production of a much higher molecular weight fraction of C_{60} polymers and broader GPC traces or larger polydispersity indices. To further prove incorporation of C_{60} in the polymer, the amount of C_{60} in polymers **3** was determined by the UV calibration method and compared with the BCBO content in the precursor polymers **2** (Table 1). It was found that the molar percent of C_{60} and BCBO matched well, except for polymer **3c** that had the highest C_{60} content (44 wt %).

All three C_{60}−PSt were readily dissolved at ambient temperatures in many common organic solvents such as $CHCl_3$, CH_2Cl_2, and THF, giving rise to a dark brown-purple solution. This solubility behavior is similar to polystyrene but unlike C_{60} itself, demonstrating the advantage of having a polymer-bonded fullerene for improved processability. The presence of C_{60} affects the property of polymer. Although the thermal stability of C_{60}−PSt **3** was comparable to that of polystyrene or BCBO−PSt **2**, as compared by their onset temperatures for 5% weight loss, the glass transition temperatures (T_g) of C_{60}−PSt **3** increased noticeably (Table 1). For example, polymer **3b** containing 9.33 mol % of C_{60} had a T_g of 156 °C, which is about 56 °C higher than that of polystyrene and 44 °C higher than that of its precursor polymer **2b**. With an increase in the C_{60} content in polymers **3**, the T_g value increased (Table 1). However, the phase separation due to the presence of large amounts of C_{60} resulted in broadening of the T_g transition as observed for **3c**.

[60]Fullerene can also be incorporated into certain polymers via the BCBO group by postpolymerization. Thus, polyethylene-*graft*-maleic anhydride[13] was readily converted to BCBO−PE **4** upon imidization with 5-aminobenzocyclobutenone in melt at about 150 °C. BCBO−PE **4** had a melting point (125 °C by DSC) slightly higher than that (122 °C) of anhydride polyethylene. Grafting of BCBO−PE **4** with an excess of C_{60} was carried out in refluxing 1,2-dichlorobenzene, yielding

light brown C_{60}−PE **5** quantitatively. Incorporation of C_{60} into polyethylene was evident by IR spectroscopy. The IR spectrum of C_{60}−PE **5** displayed a characteristic band at 528 cm^{-1} due to C_{60} and showed no peak at 1765 cm^{-1} that was seen in the IR spectrum of the starting BCBO−PE **4** (Figure 2). BCBO−PE **4** had an absorption with λ_{max} at 334 nm. For C_{60}−PE **5** this peak shifted to 314 nm and a broad absorption appeared at 370−500 nm due to the presence of C_{60}. In DSC analyses an exothermic peak was observed at 225 °C for BCBO−PE **4** due to the ring opening of BCBO but not for C_{60}−PE **5**.

In conclusion, this work has demonstrated a new approach to nearly quantitative incorporation of C_{60} into vinyl polymers based on the unique cycloaddition reaction of BCBO with C_{60}. Copolymerizability of BCBO monomer **1** with a wide range of vinyl monomers allows for the preparation of a variety of BCBO-containing polymers and thus C_{60}-containing polymers. The amount of C_{60} present in a polymer is dictated by the BCBO content in the same polymer, and the latter can be easily controlled through copolymerization or grafting.

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(12) In a typical run, a three-necked flask was charged with 100 mg of BCBO−PSt **2a**, 100 mg of C_{60}, and 10 mL of 1,2-dichlorobenzene. The resulting purple solution was then heated to reflux under nitrogen, and the reaction was monitored by IR and GPC. After 3 h, the mixture was poured into hexane to give brown solids. The unreacted C_{60} can be recovered by flash column chromatography. The solids were dissolved in toluene and precipitated from hexane again, and the same purification process was repeated several times until no more free C_{60} could be detected by GPC. After drying at 50 °C in vacuo for 24 h, polymer **3a** was obtained as brown powders.

(13) Polyethylene-*graft*-maleic anhydride, from Aldrich Chemical Co., contains ca. 0.85 wt % of maleic anhydride and is treated at 200 °C for 30 min prior to use.

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