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Direct Fullerenation of Polycarbonate via Simple Polymer Reactions

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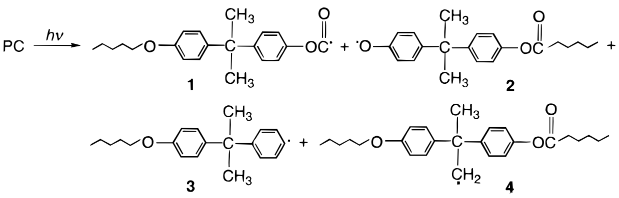
ABSTRACT: Direct fullerenation of polycarbonate (PC), a commercially important optical polymer, is achieved by simply irradiating a solution of PC and C_{60} at room temperature using a conventional UV lamp or by warming up a C_{60}/PC solution to a moderate temperature (60 °C) in the presence of AIBN, a typical radical initiator. The extent of fullerenation is controllable by varying the C_{60} feed ratio, and a fullerenated PC with a C_{60} content as high as 6.3 wt % (or more than two C_{60} molecules per PC chain) is readily prepared in almost quantitative yield (99.7%). Molecular weights of the fullerenated PCs are higher than that of the parent polymer, suggesting that the fullerenation is realized via multiaddition to C_{60}. The multiaddition, however, has not led to heavy cross-linking, and the fullerenated PCs are soluble in common organic solvents such as THF and chloroform. The fullerenation involves a radical mechanism, and its general applicability to other polymer systems is demonstrated by the ready attachment of C_{60} to poly(vinyl chloride), another commercially important polymer, by employing the AIBN-initiated fullerenation reaction.

Buckminsterfullerene may well be the most intensely researched single molecule in modern science,[1] and as a result, the buckyball has quickly proven to be not only a new carbon allotrope of aesthetic structure but also a molecule of many talents, possessing a range of exotic properties such as superconductivity, ferromagnetism, optical nonlinearity, and anti-HIV bioactivity.[2] Utilization of such properties for practical applications, however, has been largely hampered by C_{60}'s poor tractability.[3] Synthesis of fullerene polymers has attracted much interest among polymer scientists because suitably-designed fullerene polymers would be well processable and may also exhibit novel properties which are superior to those of the parent forms, thus generating new fullerene-based specialty materials. The C_{60}-containing polycarbonate (C_{60}-PC) we are going to report in this paper is actually such a nice example: It not only has much better solubility in common organic solvents but also limits strong laser pulses more effectively than does the parent C_{60}.

Thanks to the great synthetic efforts devoted by polymer chemists, many different kinds of fullerene functionalized polymers, including “pearl necklace”, “charm bracelet”, and “flagellene”, have been prepared.[4] Reaction of C_{60} with a tailor-made functional polymer, e.g., an aminated polymer, has been a popular strategy in attaching C_{60} to a polymer chain.[5] The preparation of the functional polymers, however, sometimes requires nontrivial synthetic efforts, which in turn limit the scope of applicability of the methodology. We are interested in developing *simple* polymer reactions with *general* applicability for *directly* attaching C_{60} to preformed polymers, especially those commercially-important tonnage polymers. PC is an excellent optical polymer, whose fullerenation, however, has never been studied. We here demonstrate that we can fullerenate PC in a one-pot experimental procedure by simply irradiating a solution of C_{60} and PC using a conventional UV lamp, or by warming up a C_{60}/PC solution in the presence of AIBN, a typical radical initiator. The fullerenation reactions involve a radical mechanism and would have general applicability because all known polymers generate free radicals, though with variation in the rate, by radiation-induced photolysis and/or initiator-aided thermolysis.[6] The fullerenation systems are so direct and simple that they should be of general interest to a wide audience of scientists and technologists who are working on fullerene materials.

Scheme 1



Photolysis of PC has been well documented.[6] Unlike poly(methyl methacrylate), which degrades catastrophically upon UV irradiation, PC is photochemically relatively stable, probably due to the “energy sink” function of the aromatic rings in the polymer main chain. Photolysis of PC slowly yields radicals with the structures shown in Scheme 1.

C_{60} is known as a “radical sponge”, which readily reacts with free radicals.[7] C_{60} also undergoes photolysis reaction, generating C_{60} radical ions via disproportionation of photoexcited triplet C_{60}.[8] Thus irradiation of a solution of C_{60} and PC might steadily attach C_{60} to PC chains. To check whether the fullerenation reaction would really occur, we irradiated a 5% solution of C_{60} and PC (weight ratio of C_{60} to PC: 1.08:100) using a UV lamp at room temperature under an atmosphere of dry dinitrogen for 35 h.[9] The UV irradiation gradually changed the color of the C_{60}/PC solution from purple to red and then to brown. We isolated and purified the photolysis product by repeated precipitation in hexane,

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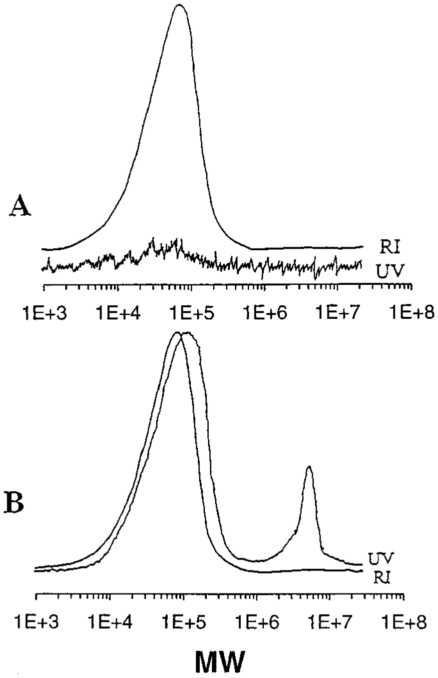


Figure 1. GPC traces of photolysis products of 1,1,2,2-tetrachloroethane solutions of PC (A) in the absence and (B) in the presence of C_{60} (samples from Table 1, no. 2 and note e, respectively). Wavelength of the UV detector in the GPC system: 340 nm.

a solvent of C_{60}[3a] but not a solvent of the polymer.[10] We collected the hexane supernatant, from which we recovered neither unreacted C_{60} nor low molecular weight C_{60} derivatives, suggesting that all the C_{60} had reacted with the polymer. The pure PC is white, but the isolated photolysis product was brown in color. The product was completely soluble in THF, which is not a solvent of C_{60},[3a] indicating that there was no unreacted C_{60} particles physically trapped inside the product and that cross-linking reactions, if any, had not gone to such an extent as to produce insoluble gels. GPC analysis of the THF solution of the photolysis product gave flat base lines in the molecular weight region around 720, where C_{60}, if any, should be detected by the refractive index (RI) and especially the UV detectors. The UV detector in the GPC system with a working wavelength of 340 nm, where C_{60} absorbs but PC almost does not, detected two intense peaks in the high molecular weight region (Figure 1B). The photolysis product obtained from a control experiment using a pure PC, however, hardly exhibited any GPC-UV peaks (Figure 1A). All the above experimental observations led to such a conclusion that all the C_{60} had been covalently attached to the PC chains, which allowed us to estimate on the mass basis that the C_{60} content of the fullerenated PC was 1.16 wt %. Calibration of the GPC-RI curve of the fullerenated PC by polystyrene standards gave a M_n of 27 000 (Table 1, no. 2), which was about two times that of the starting polymer (13 900). The average number of C_{60} molecules per PC chain calculated on the basis of the M_n data was 0.44; that is, 44 buckyballs were attached to 100 PC chains on the average.

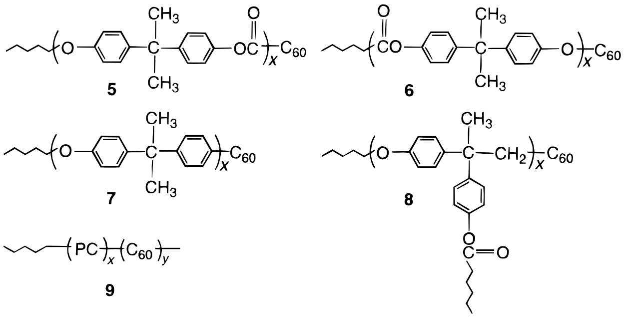
Since the UV irradiation did prove to work, we further investigated the radiation-induced fullerenation behavior. Shortening the irradiation time from 35 to 6 h resulted in a somewhat higher yield of the fullerenated PC (cf. Table 1, nos. 2 and 1), probably due to less weight loss from the CO_2 liberation during the shorter irradiation time (cf. Scheme 1; generation of **3** involving the loss of a molecule of CO_2 from **1**). The C_{60} content was lower (0.46 wt % or 0.1 C_{60}/PC chain) because the irradiation time was not long enough to attach all the C_{60} to the PC chains.[11] The unreacted C_{60} was easily separated by precipitating a THF solution of the photolysis product through a fine filter into a large amount of hexane. Doubling the C_{60} feed ratio from 1.08 to 2.16 while keeping the irradiation time unchanged (35 h; cf. Table 1, nos. 2 and 3) doubled the C_{60} content of the fullerenated PC. A further increase in both the C_{60} feed ratio and the irradiation time attached more than 2 buckyballs to a PC chain on the average.[11] Thus the degree of fullerenation can be fine "tuned" by changing the simple reaction parameters, such as feed ratio and irradiation time.

Table 1. Radiation-Induced Fullerenation of PC[a]

			fullerenated PC				
						C_{60} content	
no.	C_{60}/PC feed ratio (wt %)	irradn time (h)	yield (%)	M_n[b] (g/mol)	M_w/M_n[b]	(wt %)[c]	(no./chain)[d]
1	1.08	6	94.3	16 400	1.8	0.46	0.10
2[e]	1.08	35	92.6	27 000	2.3	1.16	0.44
3	2.16	35	82.7	23 500	2.4	2.61	0.85
4	4.98	56	76.3	28 800	1.9	5.76	2.30

[a] Irradiated in 1,1,2,2-tetrachloroethane at room temperature under dinitrogen using a 200-W Hg lamp. [b] Determined by GPC (RI detector) on the basis of a polystyrene calibration. For the starting PC, M_n = 13 900, M_w/M_n = 2.4. [c] Estimated by UV analysis at 350 nm. [d] Estimated from M_n. [e] In a control experiment, irradiation of a PC solution (50 mg/mL) in the absence of C_{60} for 35 h gave a photolysis product with M_n = 24 400, M_w/M_n = 2.4; yield: 94.3%.

Scheme 2



Although much needs to be done in understanding the details of the reaction mechanisms, the major steps in the fullerenation might involve (i) generation of the PC and C_{60} radicals by the UV irradiation and (ii) cross-reactions among the PC (radicals) and C_{60} (radicals), i.e., $PC^{\bullet} + C_{60}$, $C_{60}^{\bullet} + PC$, and/or $PC^{\bullet} + C_{60}^{\bullet}$, yielding fullerenated PCs of the possible structures shown in Scheme 2.

All the fullerenated PCs had higher molecular weights than the starting polymer ($M_n = 1.4-1.8\ M_{n,o}$), suggesting that multiaddition to C_{60} had taken place ($x > 1$). The multiaddition, however, was well under control and had not led to cross-linking, as evidenced by the high solubility of the fullerenated PCs in organic solvents such as 1,1,2,2-tetrachloroethane, THF, and chloroform. Product **9** with $x > 1$ and $y > 1$, in which several PC chains are linked by a few buckyballs, would have a very high molecular weight and might be responsible for the UV peak on the right side of the GPC curve of the fullerenated PC (cf. Figure 1B). The amount of such product, however, should be quite small, as evidenced by the weak UV peak and also by the fact that its existence could not even be detected by the RI detector.

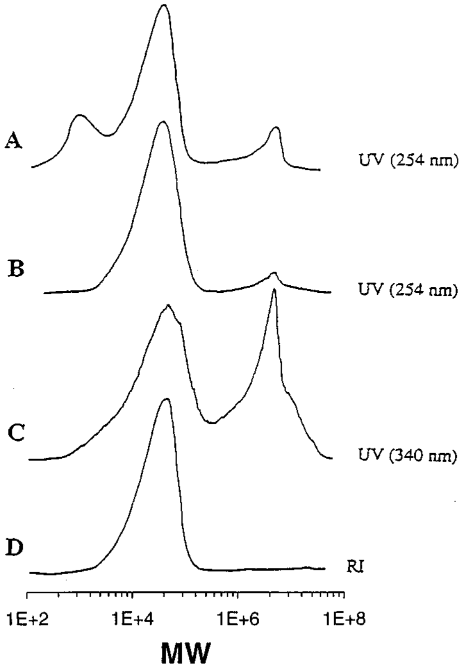


Figure 2. GPC traces of AIBN-initiated fullerenation products of PC purified (A) by precipitation in hexane and (B–D) by repeated precipitation in methanol (sample from Table 2, no. 3).

Table 2. AIBN-Initiated Fullerenation of PC[a]

			fullerenated PC				
						C_{60} content	
no.	C_{60}/PC feed ratio (wt %)	AIBN (mg/mL)	yield (%)	M_n[b] (g/mol)	M_w/M_n[b]	(wt %)[c]	(no./chain)[d]
1[e]	0.99	0.56	94.0	30 200	2.1	0.78	0.33
2	0.99	2.28	93.3	24 900	2.4	1.04	0.36
3	5.00	0.38	99.7	27 000	2.1	6.30	2.37

[a] Heated at 60 °C in 1,1,2,2,-tetrachloroethane under dinitrogen for 24 h. [b] Determined by GPC (RI detector) on the basis of a polystyrene calibration. For the starting PC, $M_n = 13\,900$, $M_w/M_n = 2.4$. [c] Estimated by UV analysis at 350 nm. [d] Estimated from M_n. [e] In a control experiment, a PC solution (50.6 mg/mL) without C_{60} was heated at 60 °C in the presence of AIBN (0.56 mg/mL) for 24 h, giving a product with $M_n = 27\,400$, $M_w/M_n = 2.2$; yield: 97.3%.

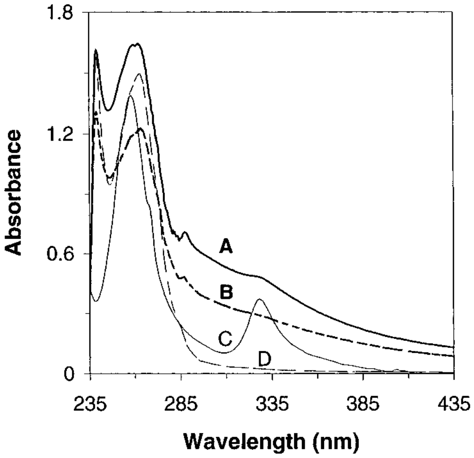


Figure 3. UV spectra of THF solutions of fullerenated PCs prepared by (A) radiation-induced and (B) AIBN-initiated fullerenation reactions (samples from Table 1, no. 4 and Table 2, no. 3, respectively). Concentration (mg/mL): (A) 0.300; (B) 0.275. UV spectra of (C) a hexane solution of C_{60} (0.011 mg/mL) and (D) a THF solution of PC (0.574 mg/mL) are also shown for comparison.

Encouraged by the radiation-induced fullerenation results, we further explored possibilities of generating radicals by other simple means. Pyrolysis is a simple way to produce polymer radicals, and we attempted to fullerenate PC by heating up a membrane of C_{60} and PC (prepared by solution casting) to 340 °C under dinitrogen. Fullerenation did occur, but unfortunately, most of the dark brown fibrous products isolated even after a short reaction time (e.g., 0.75 h) were insoluble, probably due to the uncontrolled multiaddition of PC chain radicals to C_{60} at the high temperature. Radical initiators have often been used to generate polymer radicals at moderate temperatures,[6,12] and we thus heated a C_{60}/PC solution in the presence of AIBN under dinitrogen at a relatively low temperature (60 °C) in the hope of generating PC radicals in a controlled manner.[13] The low-temperature process predominantly produced soluble products with only a trace amount (<1%) of insoluble gel being formed. The insoluble part was easily separated by filtration. The soluble main products gave three GPC-UV peaks (Figure 2A): two peaks in the high molecular weight region as observed in Figure 1B plus one new peak in the low molecular weight region. It is known that C_{60} reacts with AIBN.[7,14] We conducted a control experiment to confirm that the low molecular weight peak was from C_{60}-AIBN adducts, which were soluble in methanol. We thus repeatedly precipitated THF solutions of the reaction product into methanol, which eventually removed the low molecular weight peak, as shown in Figure 2B. The extent of fullerenation could be controlled by varying the C_{60} feed ratio (Table 2). The fullerenation yields were generally higher than those in the UV irradiation system, suggesting that, in the AIBN-initiated fullerenation system, the PC radicals were predominantly generated by the hydrogen abstraction (yielding radical **4**) but not by the CO_2 liberation (forming radical **3**). All the AIBN-initiated fullerenation reactions yielded some small amount of insoluble products, indicating that heavier multiaddition than in the UV irradiation system might have taken place. This was evidenced by the observation that the GPC-UV peak (at 340 nm) in the very high molecular weight region in Figure 2C was more intense than that in Figure 1B. As discussed later, the glass transition temperature (T_g) difference between the fullerenated PCs prepared by the two different systems further supported this conclusion.

The fullerenated PCs were characterized by spectroscopic methods. The ^1H and ^{13}C NMR spectra of the fullerenated PCs were essentially the same as those of the parent polymer, indicating that the amount of C_{60} incorporated into the PC chains was too small to be detected by the spectrometer[7,14] and confirming that the polymer had not suffered from catastrophic degradation during the fullerenation reaction but had maintained its basic polycarbonate structure. Not much change was detected by the FTIR spectrometer either, except a new weak absorption band at 528 cm^{-1}, which is believed to be from the C_{60} moiety[15] in the fullerenated PC. Electronic absorption spectra of the fullerenated PC, however, were more informative. C_{60} absorbs at 257.9 nm while PC absorbs at 262.8 nm (cf. Figure 3C and D). A dilute THF solution of a fullerenated PC prepared by the UV irradiation system showed two absorption peaks at 259.4 and 262.0 nm (Figure 3A), confirming the incorporation of C_{60} into the PC chains. A small new peak appeared at 287.2 nm. We have noticed that C_{60}- and C_{70}-styrene copolymers also show small new peaks around this wavelength,[14c] and we thus suspect that the peak might be due to the $\pi-\pi$ interaction

Table 3. T_g of Fullerenated PC[a]

no.	reaction system	C_{60} content (wt %)	T_g (°C)
1	(ctrl)	0	146.0[b]
2	UV	1.16	135.4
3	UV	2.61	142.3
4	AIBN	0.78	146.9
5	AIBN	6.30	151.1

[a] Measured by DSC at a heating rate of 20 °C/min under dinitrogen. [b] Literature data: $T_g = 145-149$ °C (ref 10).

between the buckyballs and the polymer chains. C_{60} shows a well-structured peak at 328.4 nm, but the fullerenated PC only showed a shoulder at ca. 329.5 nm, indicating that C_{60}'s electronic structure had been modified by the reaction with the PC molecules. The UV spectrum of the fullerenated PC prepared by the AIBN system was similar, except that the peaks at ca. 258 and 329 nm became weaker shoulders (Figure 3B), probably because the C_{60} in this reaction system had been subjected to heavier multiaddition (vide supra). Interestingly, at high concentrations, the UV spectra of the fullerenated PCs became completely structureless and continuously red-shifted with the increase in concentration.[16]

Several groups have reported that when C_{60} content increases, the T_g of their C_{60}-containing polymers increases regularly, decreases slightly, or almost does not change.[5e,17] In our case, the fullerenated PCs prepared by the UV irradiation system had lower T_g's than that of the parent polymer. The T_g of the fullerenated PC with a low C_{60} content (1.16%) was about 10 °C lower than that of the pure PC (cf. Table 3, nos. 2 and 1). Increasing the C_{60} content to 2.61% increased the T_g of the fullerenated PC to 142.3 °C. Similarly, the T_g for the fullerenated PC prepared by the AIBN system was low (146.9 °C) when its C_{60} content was low (0.78%) and became higher when its C_{60} content increased (Table 3, no. 5). The T_g change with C_{60} content might be explained in terms of "plasticizing" and "reinforcing". When the C_{60} content is low, the giant three-dimensional buckyballs may act as plasticizers, which increases the free volumes among the polymer chains, enabling the segmental movements or glass transition at relatively low temperature. However, when the C_{60} content increases or when a large amount of C_{60} is incorporated into the polymer system, the same buckyballs may change to function as reinforcers. Many polymer chains and/or several parts of a polymer chain might be linked by the C_{60} molecules, which would restrict the segmental movements, thus increasing the T_g of the polymer. The fullerenated PCs prepared by the AIBN system had higher T_g's than those prepared by the UV system. This might be because more PC chains are held together by C_{60} molecules in the products prepared by the AIBN-induced fullerenation, as discussed above.

The UV-induced and AIBN-initiated fullerenation reactions are inspiring because many polymers generate radicals upon UV irradiation and/or gentle heating in the presence of AIBN. In other words, the radical-mediated fullerenation may prove to be a simple and general methodology for preparing C_{60}-containing polymers. To check the general applicability of the fullerenation reactions, we warmed up a 2.8% chlorobenzene solution of poly(vinyl chloride) (PVC) and C_{60} (weight ratio of PVC to C_{60}: 100:4.99) to 60 °C in the presence of AIBN (0.13%) under dinitrogen for 24 h. The simple gentle heating steadily attached about four C_{60} molecules to a PVC chain,[16c] demonstrating the versatility of the AIBN-initiated fullerenation.

In summary, in this study, we have developed radiation-induced and initiator-aided fullerenation reactions for functionalizing PC, a commercially important optical polymer. The fullerenation has the following noteworthy features: (i) It involves *direct* reaction between C_{60} and a preformed polymer, thus obviating the need for preparing functionalized polymers and/or C_{60} derivatives. (ii) It involves a *simple* one-pot experimental procedure. Simply irradiating a C_{60}/PC solution at room temperature or mildly warming up a C_{60}/PC/AIBN solution to a moderate temperature (60 °C) can steadily attach more than two C_{60} molecules to a PC chain. (iii) It involves a radical mechanism. It thus should have *general* applicability and should in principle work for any polymers that generate radicals upon UV irradiation and/or thermal treatment in the presence of a radical initiator, as demonstrated in the case of PVC fullerenation. The fullerenated polymers functioned as excellent optical limiters. For example, at the same linear transmittance of 33% to 8-ns, 532-nm laser pulses, the transmitted fluence from a THF solution of a fullerenated PC (sample from Table 1, no. 4) at an incident fluence of 1826.2 mJ/cm^2 was 173.5 mJ/cm^2.[18] This value was two times lower than that (353.5 mJ/cm^2) from a toluene solution of C_{60}; that is, the fullerenated PC is a much better optical limiter than the parent C_{60}. The fullerenated polymers with different C_{60} contents could filter light of any wavelength in almost the entire UV and visible spectral region, a truly unusual property which has not been found in any other existing materials including the parent C_{60}.[16] Thus the fullerenation not only provides a versatile synthetic tool for preparing processable fullerene polymers but also offers attractive opportunities for exploring new fullerene-based specialty materials with unique properties that are not found in the parent forms.

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(9) Into a baked 50-mL two-necked round-bottomed flask were added 500.6 mg of PC (Aldrich; further purified by precipitation in our laboratory), 5.4 mg of C_{60} (99.95%, MER), and 10 mL of 1,1,2,2-tetrachloroethane. After all the PC and C_{60} were completely dissolved, 7 mL of the homogeneous solution was transferred to a quartz tube and degassed with prepurified dry dinitrogen three times. The solution was irradiated with a 200-W Hg lamp (Oriel) under dinitrogen with continuous stirring. After 35 h of irradiation, a small aliquot was syringed out from the reaction mixture and precipitated into 5 mL of hexane. The clear colorless supernatant was separated from the precipitated polymer through a filter, and the polymer was washed with hexane several times. The supernatant and washing hexane were combined together in a flask and evaporated using a rotary evaporator. No visible solids were left in the evaporation flask. One milliliter of toluene (a solvent of C_{60}) was nevertheless added to the flask, and UV analysis showed no absorption peaks from unreacted C_{60}, confirming that all the C_{60} had reacted. The whole reaction mixture was then precipitated into 1 L of hexane through a filter paper. No solid particles were left on the filter paper, indicating that no insoluble cross-linking products formed during the photolysis reaction. The precipitated polymer was filtered off using a Gooch crucible, washed with hexane, and dried at room temperature. The isolated polymer was redissolved in THF, which is not a solvent of C_{60},[3a] and the resulting THF solution was reprecipitated into hexane through a filter paper. No particles were left on the filter paper, and the hexane supernatant was colorless, confirming that all the C_{60} had been incorporated into the polymer chains. The precipitated polymer was filtered off and thoroughly dried under high vacuum to a constant weight to give a brown powder. Yield: 92.6%. C_{60} content: 1.16 wt %. M_n = 27 000 g/mol, $M_w/M_n = 2.3$. UV (0.3 mg/mL in THF) λ_{max}: 238.9, 259.4, 262.0, 287.2, 329.5 (sh) nm. IR (KBr) υ: 3040 (w), 2968 (s), 1778 (vs), 1602 (m), 1506 (s), 1410 (m), 1386 (w), 1364 (m), 1230 (vs), 1194 (s), 1162 (s), 1080 (s), 1014 (s), 888 (m), 830 (s), 768 (m), 556 (s), 528 (w) cm^{-1}.

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(11) Since all the C_{60} in reactions 2 and 3 (Table 1) had been attached to PC, we used a calibration curve based on the UV absorption data of the two samples at 350 nm[4,5] to estimate the C_{60} contents of the fullerenated PCs from reactions 1 and 4, in which not all the C_{60} had reacted.

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(13) Into a 25 mL flask containing 506 mg of PC and 5 mg of C_{60} was added 10 mL of 1,1,2,2-tetrachloroethane. After all the PC and C_{60} were dissolved, 5.6 mg of AIBN was added and the solution was degassed with dinitrogen three times. Stirring at 60 °C under dinitrogen for ca. 1 h changed the color of the solution from purple to brown. After 24 h, a similar method as detailed above (cf. note 9) was employed to confirm that no unreacted C_{60} was left in the reaction system. The reaction mixture was then added dropwise through a filter paper to 1 L of hexane. A trace amount (<1%) of insoluble gel was left on the filter paper. The precipitated crude product was filtered off and dried under vacuum. The crude product showed three GPC-UV peaks with one located in the low molecular weight region. Repeated precipitation in hexane could not remove the low molecular weight peak, indicating that the peak was not from unreacted C_{60}. We suspected that the peak might be from byproducts of the reactions between C_{60} and AIBN, and we carried out a control experiment in which a C_{60}/AIBN solution (without PC) was heated under identical conditions. The isolated product showed a GPC-UV peak in the same molecular weight region, confirming that the low molecular weight peak was indeed from the C_{60}-AIBN adducts. We checked the solubility of the adducts and found that they were soluble in methanol. We thus redissolved the crude fullerenation product in ca. 10 mL of THF, and the resulting solution was reprecipitated through a filter into 1 L of methanol. The precipitation was repeated several times until GPC analysis showed no peaks in the low molecular weight region. The finally purified product was thoroughly dried at room temperature under high vacuum to a constant weight to give a brown powder. Yield: 94.0%. M_n = 30 200 g/mol, $M_w/M_n = 2.1$. The UV and IR spectra of the product were similar to those of the fullerenated PC prepared by the radiation-induced fullerenation reaction (cf. note 9).

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